

CHAPTER III
RESULTS, DISCUSSION AND CONCLUSION

3.1 General Features

3.1.1 Solid spectra (Figs. 2 and 3)

There are many peaks in the C=O and C=C=C stretching region; they are probably due to :

- (i) Polymeric species in M(II)
- (ii) Combination bands and overtones in M(II) and M(III)
- (iii) Ligand-crystal field effects:-

(a) coupling interactions of acetylacetonate rings in M(II) and M(III)

(b) Jahn-Teller effect in M(III)

The above will now be briefly outlined.

(i) Polymeric species in M(II) (Figs. 1E, 1F and 1G)

Cu(II) forms dimer and the monomer is planar, symmetry D_{2h} . Ni(II) and Mn(II) are believed to have identical structures, both are trimeric.¹⁹ In Ni(II) there are nine possible structures of trimers alone.¹⁷ Ni(II) and Mn(II) monomers are planar, symmetry D_{2h} .

Zn(II) is also trimeric, but the monomer is tetrahedral, symmetry C_{2v} . Co(II) forms tetramers, the monomer is also tetrahedral, symmetry C_{2v} . Polymeric species assignments will be discussed later.

(ii) Combination bands and overtones in M(II) and M(III)

This may lead to Fermi resonance, which will be discussed later.

(iii) Ligand-crystal field effects

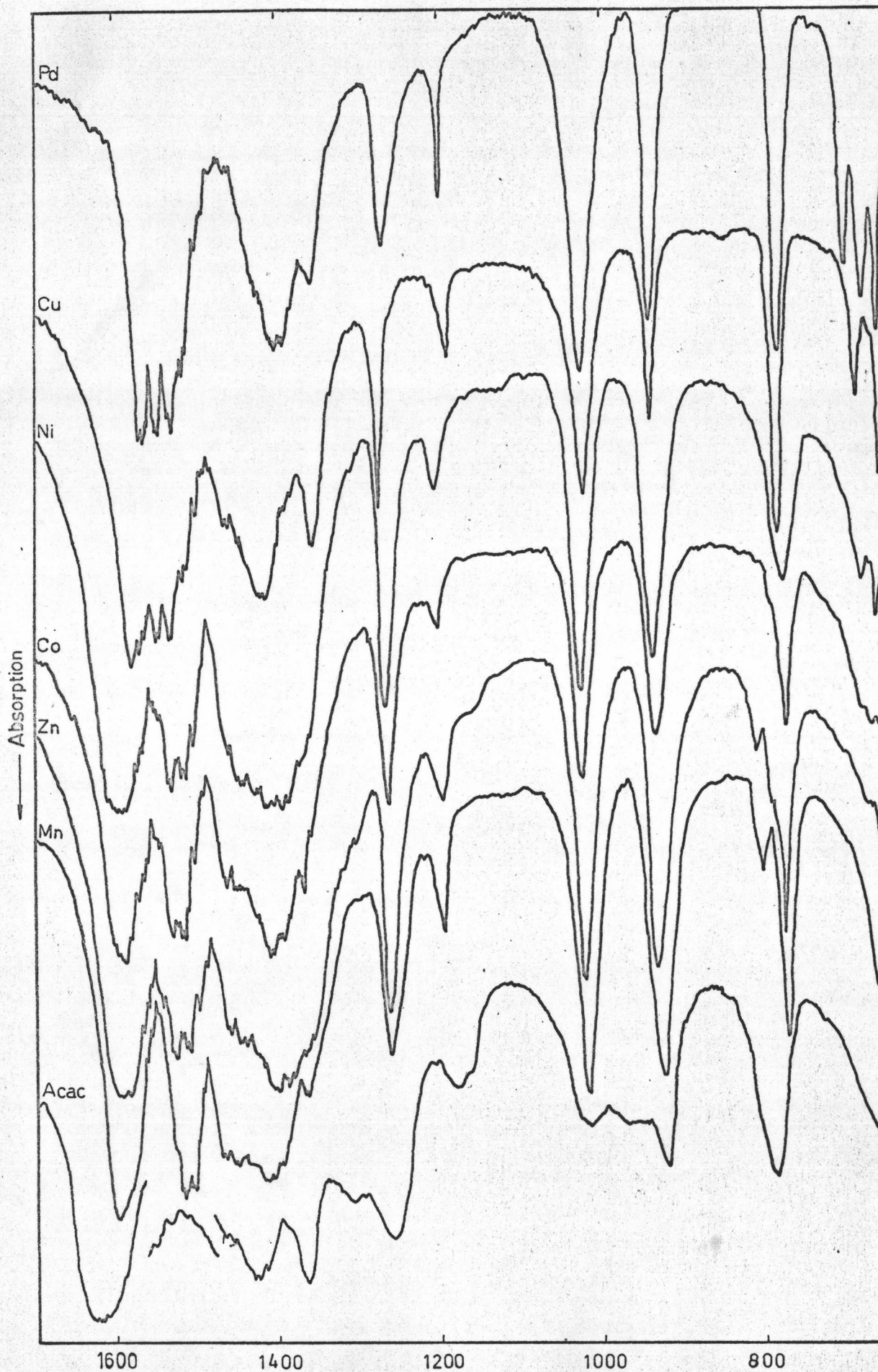


Fig. 2 Infrared spectra of acetylacetonates of divalent metals.

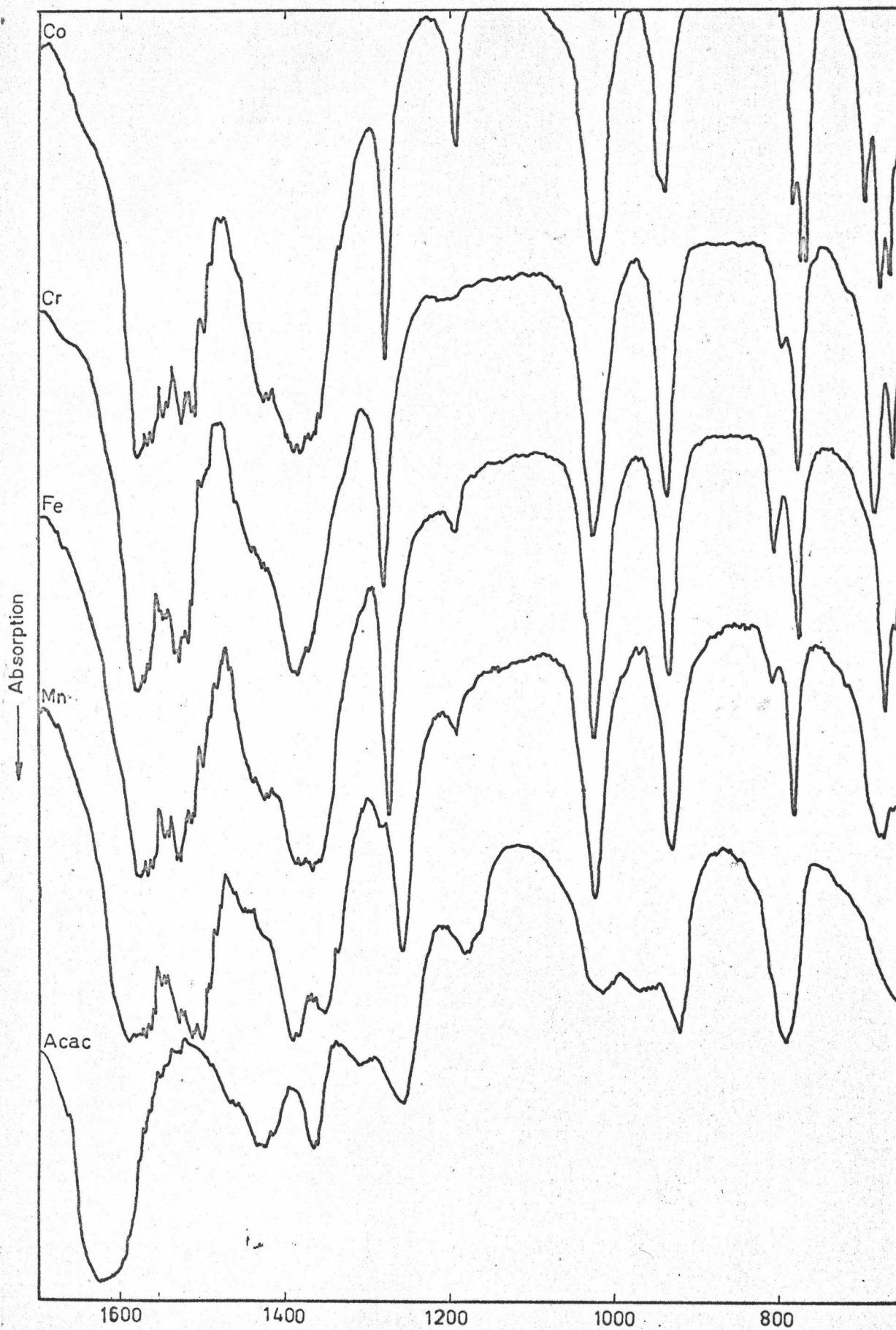


Fig. 3 Infrared spectra of acetylacetonates of trivalent metals.

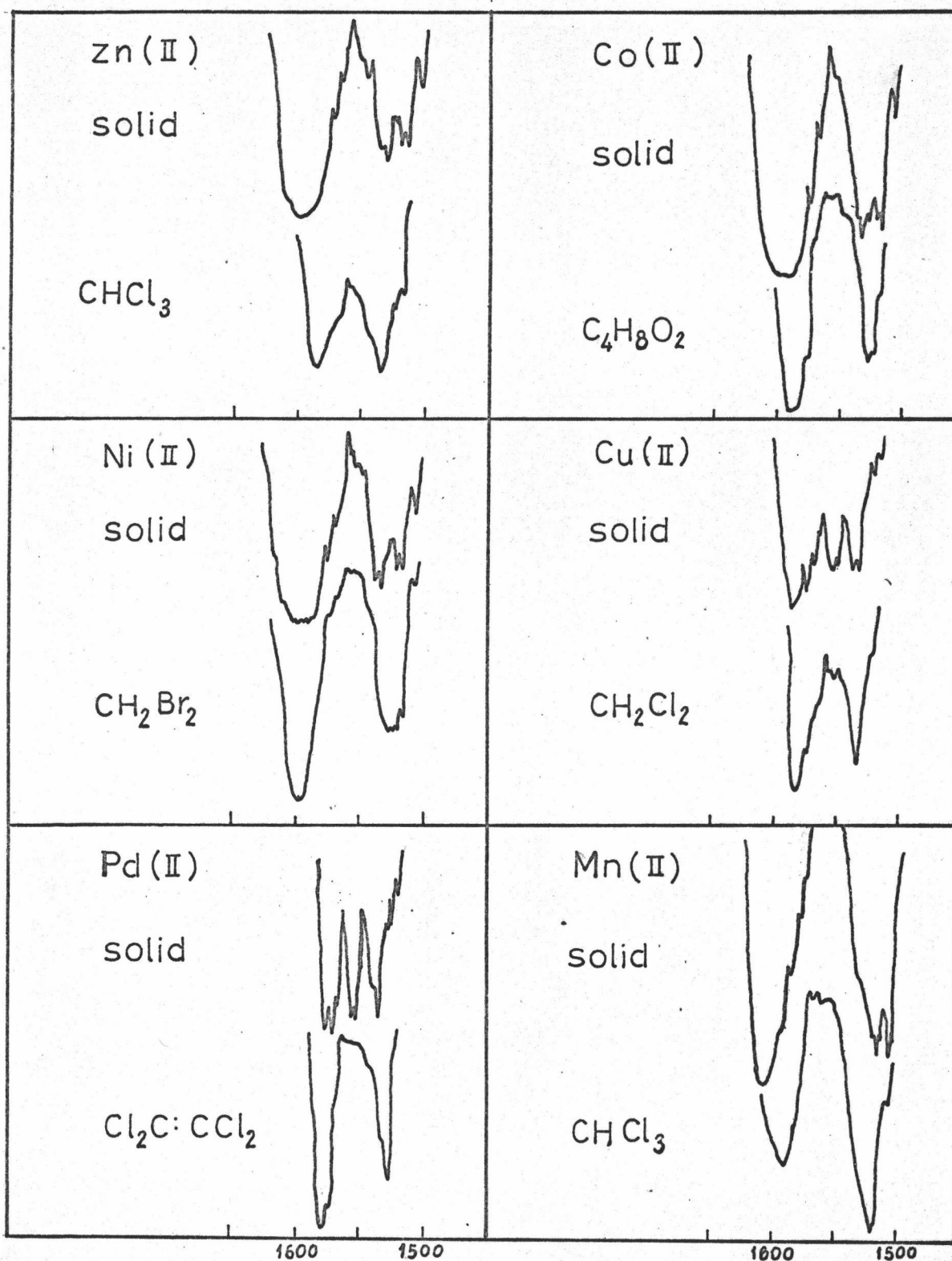


Fig. 4 Typical solution spectra of
M(II) acetylacetonate.

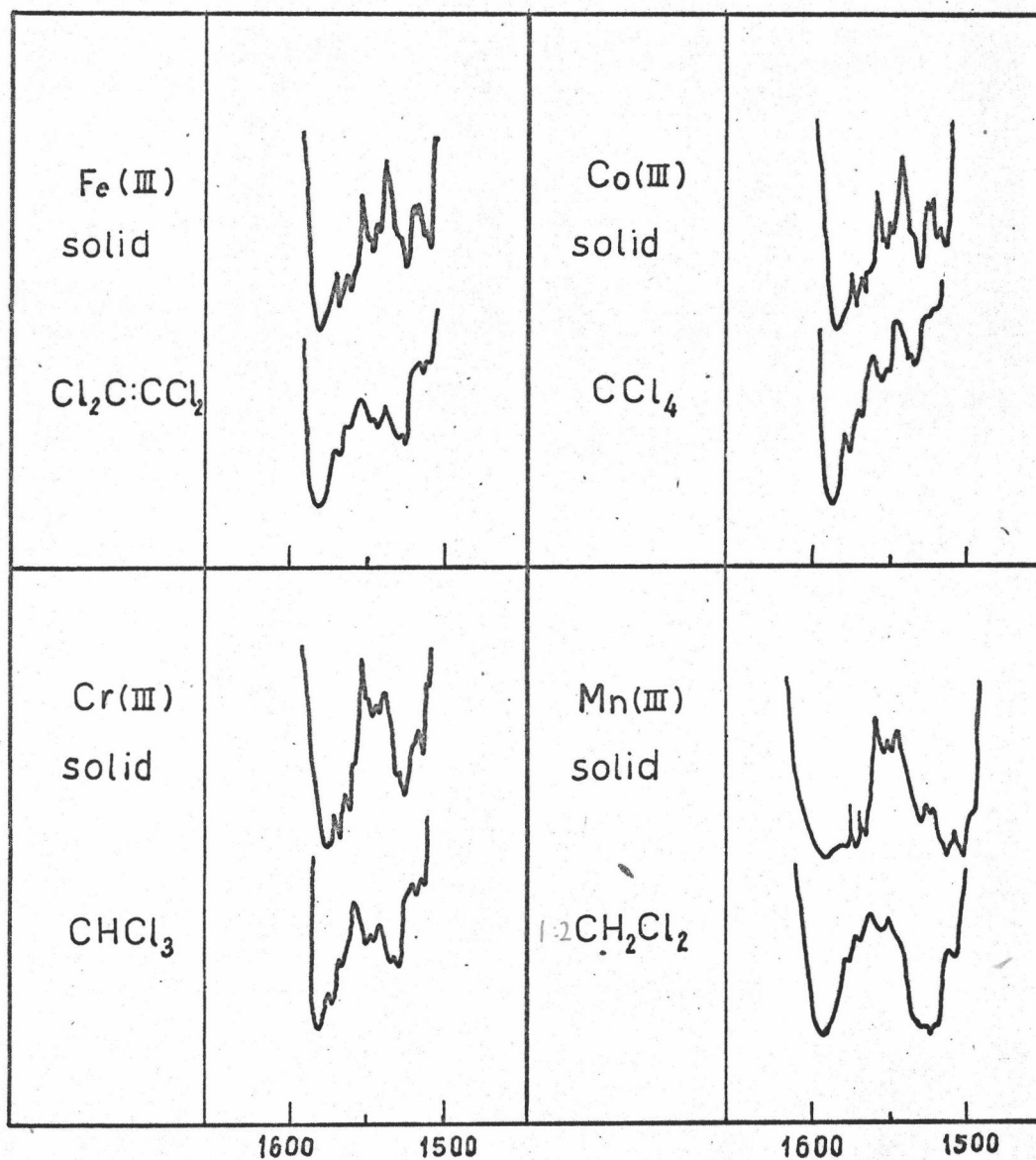


Fig. 5 Typical solution spectra of
M(III) acetylacetonate.

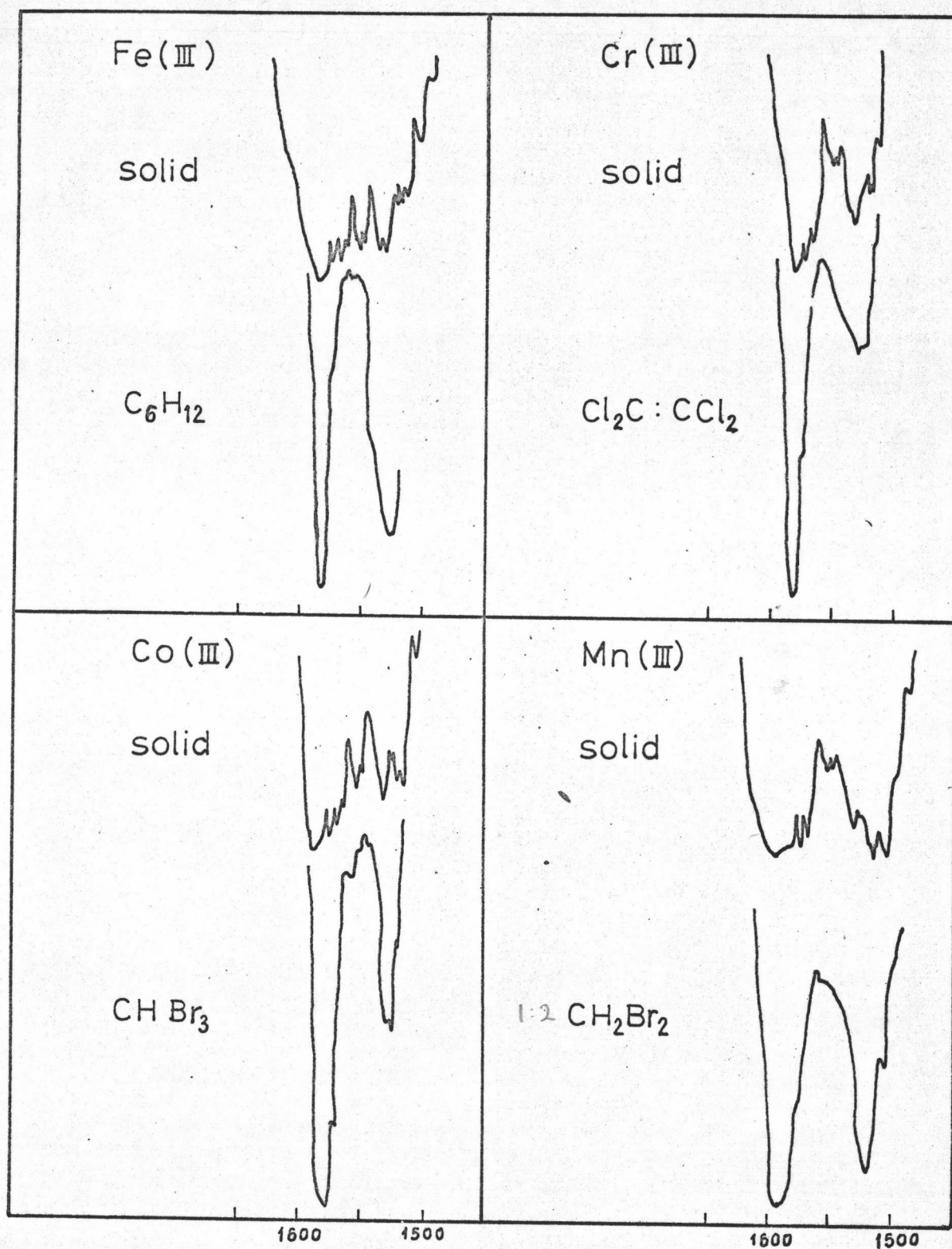


Fig. 6 Jahn-Teller effect in M(III) acetylacetonate.

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(a) Coupling interactions among the chelate rings in M(II) and M(III) undoubtedly exists, although they may not be strong at the $\approx 1600 \text{ cm.}^{-1}$ region.

(b) Jahn-Teller effects in M(III): The local symmetry of the planar ring is C_{2v} which corresponds to the molecular point group, the over all molecular symmetry is D_3 , which corresponds to the unit cell group. These two groups are linked together by a common subgroup C_2 , the site group in crystals.

It is possible to have Jahn-Teller splitting, due to the distortions of the unit cell $D_3 \rightarrow C_2$. This will also be discussed later.

3.1.2 Solution spectra (Figs. 4,5, and 6)

They are greatly simplified, because the three effects mentioned in the solid spectra are now much less effective in dilute solutions. In very dilute solutions, 10^{-3} - $10^{-4}M$, only monomeric species in M(II) should exist.²⁹ Also Jahn-Teller effects should be completely removed in M(III) in dilute solutions. Our selected solution spectra bear this out (Fig. 6)

3.1.3 Solvent shifts: C=O and C=C=C stretching vibrations.

Table 1 shows the solvents are numbered according to decreasing order of dipole moments, solvent numbered 13-20 are all non-polar.

From Table 2-11, it can be seen that the shifts $\Delta \nu$ are independent of solvent properties, e.g., dipole moment, μ ; dielectric constant ϵ ; refractive index, n ; and polarizability α . This solvent independency is contrary to all reports on stretching vibrational shifts in the organic and inorganic systems, e.g.,

Table 1 Solvents in decreasing dipole moment⁽¹⁾

Solvents	Dipole moment (Debye units)
1. Cyclohexanone ⁽²⁾	2.8
2. Pyridine	2.22-2.23
3. Dichloromethane	1.57
4. Dibromomethane ⁽²⁾	1.42
5. Dichloroethane	1.32
6. Bromoform ⁽²⁾	1.3
7. Diethylether	1.17
8. Chloroform	1.1
9. Dibromoethane	1.0
10. o-Xylene	0.58
11. Toluene	0.4
12. m-Xylene	0.37
13. Benzene	0
14. Carbontetrachloride	0
15. Cyclohexane	0
16. Dioxane	0-0.4
17. n-Hexane	0
18. Methylcyclopentane	0
19. Tetrachloroethylene	0
20. p-Xylene	0

(1): Smyths, Charles Phelps, "Dielectric Behaviour and Structure",
McGraw-Hill Book Company, New York (1955).

(2) Trans. Farad. Soc., 1934, 30, appendix.

Table 2 Solvent shifts of copper (II) acetylacetonate (cm.^{-1})

Solvents	ν_8			ν_1	ν_9	ν_{10}	ν_2
	1586		1552	1534	1464	1415	1280
		$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
2	-	-	-	+2	-	-	+2
3	1582	+4	-1	+3	-	-	-
4	1582	+4	-3	+2	-	+5	-2
5	1581	+5	-	+3	-	-	-
6	1580	+6	-2	+4	-	+11	-4
8	1580	+6	-1	+4	-	+10	-
9	1580	+6	-	-	-	-	-
13	1582	+4	-	-	-	-	-
14	-	-	-	-	-	+5	-
16	1584	+2	-	+4	-	-	-
19	1584	+2	-	+5	-	-	-
$\sum \Delta\nu /n$		4.3		3.4		7.8	2.7

$$\% \text{ C}=\text{O} = 56$$

Table 3 Solvent shifts of palladium (II) acetylacetonate (cm.^{-1})

Solvents	ν_8				ν_1			ν_9	ν_{10}	ν_2
	1575		1568	1550	1531	1526*	1518	1428	1396	1276
		$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
3	-	-	+3	-5	+6	+1	+1	-	+8	-
4	-	-	+4	-4	+7	+2	+3	-	-	+2
5	-	-	+2	-6	-	+1	+1	-	+8	-
6	1575	0	0	-8	+11	+6	+2	-5	+8	0
8	1572	+3	+1	-3	-	-	+2	-	+11	-2
9	-	-	+1	-6	+9	4	+4	-	+6	-
13	1572	+3	+2	-	-	-	-	-	-	0
14	-	-	-	-	-	-	-	-	+7	-
16	1576	+1	-2	1	+7	+2	+2	-	-	-
19	1573	+2	+2	2	+12	+7	+3	-	+4	-
$\sum \Delta\nu /n$				4.4	8.7	3.3			7.5	1

$$\% \text{ C} \equiv \text{O} = 63$$

* average of 1532+1518

Table 4 Solvent shifts of zinc (II) acetylacetonate (cm.^{-1})

Solvents	ν_8		ν_1		ν_9	ν_{10}	ν_2
	1596		1531	1517	1466	1406	1268
		$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
2	-	-	-	-	-	-	-
3	1586	+10	0	0	-	-	-
4	1582	+14	+1	-	-	-	-5
5	1613	-17	-	-	-	-	-
6	1580	+16	+2	0	-	+14	-3
7	1582	+14	-	-	-	-	-
8	1583	+13	-1	-1	-	+13	-
13	1589	+7	-	-	-	-	+1
14	1585	+11	-	-	-	-	-
16	1590	+6	+5	-3	-	-	-
19	1582	+14	+3	-2	-	-	-
$\Sigma \Delta\nu /n$		12.2	2			13	3

$$\% \text{ C} = \text{O} = 86$$

Table 5 Solvent shifts of cobalt (II) acetylacetonate (cm.^{-1})

Solvents	ν_8		ν_1		ν_9	ν_{10}	ν_{12}
	1597		1532	1518	1465	1409	1266
		$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
2	-	-	-	-	-	-	-
3	1592	+5	+2	+1	-	-	-
4	1589	+8	+4	-2	-	-	-
5	-	-	0	-	-	-	-
6	1591	+6	+3	-	-	+9	-4
8	1592	+5	0	-	-	-10	-
9	1590	+7	-	-	-	-	-
13	1588	+9	-	-	-	-	-
14	1588	+9	-	-	-	+2	-
18	1584	+13	+4	-	-	-	-
$\sum \Delta\nu /n$		7.8	2.2			7	4

% C=O = 78

Table 6 Solvent shifts of nickel (II) acetylacetonate (cm.^{-1})

Solvents	ν_8		ν_1		ν_9	ν_{10}	ν_2
	1595		1533	1518	1455	1402	1266
		$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
2	-	-	-	-	+1	-	+5
3	1600	-5	+3	-	-	-	-
4	1600	-5	+2	0	-	-	-1
5	-	-	+3	-	-	-	-
6	1598	-3	+3	0	-	-7	-3
7	1602	-7	-	-	-	-	-
8	1598	-3	-	-	-	-14	-2
9	1599	-4	+9	+3	-	-	-
13	1608	-13	-	-	-	-11	0
14	1599	-4	+2	+1	-	-11	-
16	1594	+1	+9	+2	-	-	-
19	1609	-14	+5	-	-	-10	-
$\Sigma \Delta\nu /n$		5.9	4.5			10.6	2.2

$$\% \text{ C} \equiv \text{O} = 57$$

Table 7 Solvent shifts of manganese (II) acetylacetonate
(cm.^{-1})

Solvents	ν_8		ν_1		ν_9	ν_{10}	ν_2
	1605		1515	1505	1449	1412	1260
		$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
2	-	-	-1	-	-	-	+2
3	1590	+15	-5	-	-	-	-
4	-	-	-4	-	-	-	-
6	1600	+5	-	-	-	-2	-
8	1591	+14	-5	-	-	+13	-
9	-	-	-	-	-	-	+2
13	-	-	-	-	-	-	+5
$\sum \Delta\nu /n$		11.3	3.8			7.5	3

$$\% \text{ C} = 75$$

Table 8 Solvent shifts of chromium (III) acetylacetonate
(cm.^{-1})

Solvents	ν_8			ν_1		ν_9	ν_{10}	ν_2	
	1585		^{sh} 1575	^{sh} 1568	1535	^{sh} 1520	1429	1389	1281
		$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
2	-	-	-	-	0	+2	-	-	+1
3	1580	+5	+2	-	7	+1	-	-3	-
4	1581	+4	+1	+1	2	+2	-	-	+1
5	1583	+2	+1	+1	0	0	-	-3	-
6	1580	+5	-1	-1	-1	-2	+1	-3	-1
7	1583	+2	-1	-2	0	-3	-	-	-
8	1583	+2	0	0	-	-	-	-5	-3
9	1579	+6	+2	+2	1	0	-	-	-
10	1583	+2	-	-	-	-	-	-	-2
11	1583	+2	-	-	-	-	-	-	-1
13	1584	+1	-1	-1	-	-	-	-	-2
14	1582	+3	-1	-1	-	-	-	-6	0
16	1582	+3	+1	-1	+5	-	-	-	-
20	1584	+1	-1	-3	-	-	-	-	-1
$\sum \Delta\nu /n$		2.9			2			4	1.3

$$\% \text{C} = 0 = 66$$

Table 9 Solvent shifts of Manganese(III) acetylacetonate (cm.^{-1})

Solvents	ν_8				ν_7			ν_9	ν_{10}	ν_2
	1594		sh 1574	sh 1567	1531	1514	sh 1504	1425	1390	1260
		$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
2	-	-	-	-	-	-1	-	-	+6	-3
3	1591	+3	0	-2	-	-7	-2	-	-6	-
4	1591	+3	-3	-2	-	-7	0	-	-	-
5	1590	+4	-1	-1	-	-11	-3	-	-	-
6	1588	+6	+2	+2	0	-1	+1	-	-5	-3
7	1595	-1	0	0	-	-	-	-	-	-
8	1589	+5	-1	-1	+1	-	-	-	-6	-
9	1592	+2	0	0	+1	-4	-1	-	-	-
10	1586	+8	-	-	-	-	-	-	-	-4
13	-	-	-	-	0	0	-	-	-	0
14	1591	+3	-	-	-	-2	-	-	-6	-
15	1588	+6	-	-	-	-	-	-	-	-
18	1591	+3	-	-	-	-	-	-	-	-
19	1587	+7	-1	-1	-	-4	0	-	-5	-7
20	1590	+4	-	-	-	-	-	-	-	-1
$\sum \Delta\nu /n$		4.2				4.1			5.7	3

% C=O = 50

Table 10 Solvent shifts of cobalt (III) acetylacetonate
(cm.^{-1})

Solvents	ν_8				ν_1	ν_9	ν_{10}	ν_2
	1587		sh 1575	sh 1568	1523	1429	1390	1284
		$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
1	1583	+4	+2	-	-1	-	-	-
2	-	-	-	-	0	-	+1	-1
3	1581	+6	+1	0	+1	-	+1	-
4	1580	+7	+1	-1	-2	-	-	+1
5	1584	+3	0	0	+1	-	+1	-
6	1580	+7	0	-1	+2	-2	-3	-2
8	1581	+6	+2	0	-	0	+2	-1
9	1581	+6	0	-1	+1	-	-	-
10	1583	+4	+1	-	+2	-	-	-1
11	1584	+3	0	-1	-	-	-	0
13	1584	+3	0	+1	-	+1	-	+1
14	1584	+5	-1	-1	-2	-2	+2	-
15	1584	+3	-	-	-	-	-	-
16	1582	+5	+1	0	-2	-	-	-
19	1582	+5	+2	1	+1	-	-4	+1
20	1582	+5	+2	1	-	-	-	+1
$\sum \Delta\nu /n$		4.8			1.4		2	1

Table 11 Solvent shifts of iron (III) acetylacetonate (cm.^{-1}).

Solvents	ν_8			ν_1		ν_9	ν_{10}	ν_2
	1583	sh 1575	sh 1569	1532	sh 1520	1428	1385	1279
		$\Delta \nu$	$\Delta \nu$	$\Delta \nu$	$\Delta \nu$	$\Delta \nu$	$\Delta \nu$	$\Delta \nu$
1	1582	+1	-1	-	0	-	-	-
2	-	-	-	-	+1	0	-	+1
3	1587	-4	0	+1	0	0	-	-
4	1581	+2	+1	0	0	0	-	-2
5	1587	-4	0	+2	-1	-2	-	-
6	1575	+8	-	-	0	0	+2	-4
7	1585	-2	+1	+1	+1	-	-	-
8	1576	+7	+5	+2	-	-	-	-5
9	1581	+2	+1	+1	-1	-1	-	-5
10	1583	0	+1	0	+3	-	-	-
11	1585	-2	+1	+1	0	-	-	-
13	1588	-5	0	+1	0	0	-	-
14	1580	+3	0	+1	+2	-	-	-
15	1581	+2	-	-	+3	-	-	-
16	1578	+5	+3	+3	+2	0	-	-
17	1582	+1	-	-	-	-	-	-
18	1584	-1	-	-	-	-	-	-
19	1586	-3	+2	+1	-1	0	-	-
20	1587	-4	-1	-1	-	-	-	-
$\Sigma \Delta \nu / n$		3.1			1		4.6	1.2

C=O str. in $M(CO)_6^{30}$.

The reason is obvious, the divalent and trivalent metal acetylacetonates studied here are in a "bonded" system, as opposed to "free" systems so far reported in the literature. The solvent independency suggests that solvents, polar or non-polar, have similar effects in "bonded" systems. Physically it is reasonable to expect that a "bonded" system is too rigid to have large solvent shifts, $\Delta \nu$ (20 cm^{-1} plus). In extreme cases like pyrrole,³¹ the N-H solvent shifts are 30-343 cm^{-1} . This of course is a "free" system. Further, particularly in crystals, solvent molecules have less room to maneuver than in liquids.

The general features will now be discussed in more details.

3.2 Assignments of Divalent and Trivalent

Metal Acetylacetonate Complexes

Since band assignments of metal acetylacetonate complexes in the range 1600-1250 cm^{-1} are still a subject of controversy, the present work introduces solvent shift method to hopefully settle this problem.

Reasonable assumptions used in our band assignments are as follow:-

- (i) The intensities of the fundamental bands in both solid and solution are stronger than those of combination bands or overtones;
- (ii) The size of solvent shifts of fundamentals is larger than those of combination bands or overtone bands⁹;
- (iii) The frequency shifts of C=O bond are more than that

Table 12 The assignments of acetylacetonates of divalent metals
infrared absorption bands in the 1250-1750 cm^{-1} region.

Metal	Bands (cm^{-1})	Nakamoto ²¹ Shimanouchi ²⁸ (solids)	Musso ²¹ (in CHCl_3)	Bands (cm^{-1})	Present Work (solids)
Cu(II)	1580(b_2)	C=C(asy.)	C=O (sym.)	1586(a)	C=O 56%
	1554 } (a_1)	C=O(sym.)	C=C=C(asy.)	1552(a)	polymeric C=O
	1534 }			1534(b)	C=C=C 56%
	1464(b_2)	C=O+CH bend.	CH_3 deg.def.	1464(b)	CH_3 deg.def.
	1415(b_1)	CH_3 deg. def.	C=O (asy.)	1415(b)	C=O
	1274(a_1)	C=C+C- CH_3 str.	C=C=C(sym)	1280(a)	same
Pd.(II)	1570(b_2)	C=C (asy.)	Not recorded in CHCl_3	1575(a)	polymeric C=O
				1568(a)	polymeric C=O
	1547 } (a_1)	C=O (sym.)	C=O	1550(a)	C=O 63%
	1523 }		C=C=C	1531(b)	C=C=C 63%
				1518(B)	1278+259=1537
	1430(b_2)	C=O+CH bend.	CH_3 deg.def.	1428(b)	CH_3 deg. def.
	1395(b_1)	CH_3 deg.def.	C=O (asy)	1396(b)	C=O
	1273(a_1)	C=C+C- CH_3 str.	C=C=C (sym.)	1276(a)	same

Table 12 (Continued)

Metal	Bands (cm.^{-1})	Nakamoto ²⁴ Shimanouchi ²⁸ (solids)	Bands ²⁷ (cm.^{-1})	Present Work (solids)
Zn(II)	1592(b_2) 1523(b_1) 1464(b_2) 1394(b_1) 1264(a_1)	C=C (asym) C=O (sym) C=O+CH bend. CH ₃ deg. def. C=C+C-CH ₃ str.	1601(a) 1531(b) 1517(b) 1466(b) 1406(b) 1268(a)	C=O 86% C=C=C 86% polymeric C=C CH ₃ deg. def. C=O same
Co(II)	1601(b_2) 1513(a_1) 1461(b_2) 1398(b_1) 1261(a_1)	C=C (asym) C=O (sym) C=O+CH bend. CH ₃ deg. def. C=C+C-CH ₃ str.	1597(a) 1532(b) 1518(b) 1465(b) 1409(b) 1266(a)	C=O 78% C=C=C 78% polymeric C=C CH ₃ deg. def. C=O same

Table 12 (Continued)

Metal	Bands (cm.^{-1})	Nakamoto ²¹ Shimanouchi ²⁸ (solids)	Bands ²⁴ (cm.^{-1})	Present Work
Ni(II)	1598(b_2) 1514(a_1) 1453(b_2) 1398(b_1) 1261(a_1)	C=C (asym) C=O (sym) C=O+CH bend. CH ₃ deg. def. C=C+C-CH ₃ str.	1595(a) 1533(b) 1518(b) 1455(b) 1402(b) 1266(a)	C=O 57% C=C=C 57% polymeric C=C CH ₃ deg. def. C=O same
Mn(II)			1605(a) 1515(b) 1505(b) 1449(b) 1412(b) 1260(a)	C=O 75% C=C=C 75% polymeric C=C CH ₃ deg. def. C=O C=C=C

Table 13 The assignments of acetylacetonates of trivalent metals infrared absorption bands in the 1250-1750-cm⁻¹ region.

Metal	Bands (cm ⁻¹)	Nakamoto, ²¹ Shimanouchi ¹⁸ (solids)	Pinchas ²⁶	Bands (cm ⁻¹)	Present Work (solids)
Cr(III)	1575(b ₂)	C=C (asym)	Partial C=O	1582(e)	C=O 66%
	1524(a ₁)	C=O (sym)	C=C	1578 (A ₁ +E) 1568	922+657=1572 or J-T
	1427(b ₂)	C=O + CH bend	CH ₃ deg.def.	1554(A ₁ +E)	1281+277=1558; 790+774=1564 or J-T
	1385(b ₁) 1281(a ₁)	CH ₃ deg.def. C=C + C-CH ₃ str.	Another CH ₃ deg.def.? C=C + C-CH ₃ str.	1535(e, a ₂) 1520(E)	C=C=O 66% 1198+307=1505 or J-T
Mn(III)	1576(b ₂)		Partial C=O	1594(e)	C=O 50%
				1574	1016+566=1582 or J-T
				1567	654+925=1579 or J-T
				1552 1531	1282+270=1552 or J-T 1254+270=1524 or J-T

Table 13 (continued)

Metal	Bands (cm^{-1})	Nakamoto, ²¹ Shimanouchi ²⁸ (solids)	Pinchas ²⁶	Bands (cm^{-1})	Present Work (solids)
Fe(III)	1572(b_2)	C=C (asym)		1583(e)	C=O 76 %
				1575	932+662=1584 or J-T
				1569 (A_1+E)	1191+373=1564 or J-T
				1552	1276+273=1549; 895+662=1557 or J-T
	1526(a_1)	C=O (sym)		1532(e, a_2)	C=C 76 %
	1425(b_2)	C=O + CH bend		1520(A_1+E)	768x2=1536 or J-T
	1390(b_1)	CH_3 deg.def.		1428(e, a_2)	CH_3 deg.def.
1276(a_1)	C=C + C- CH_3 str.		1385(e, a_2)	C=O	
			1279(e)	same	

Table 13 (continued)

Metal	Bands (cm^{-1})	Nakamoto, ²¹ Shimanouchi ²⁸ (solids)	Pinchas ²⁶	Bands (cm^{-1})	Present Work (solids)
Mn(III)	1510(a_1)		C=C	1514(e, a_2)	C=C-C 50 %
	1422(b_2)		CH ₃ deg.def.	1504(A_1+E)	592+925=1517 or J-T CH ₃ deg.def.
	1380(b_1)		Another CH ₃ deg.def.?	1448(e)	C=O
	1254(a_1)		C=C + C-CH ₃ str.	1390(e, a_2)	same
Co(III)	1578(b_2)	C=C (asym)		1587(e)	C=O 77 %
	1527(a_1)	C=O (sym)		1575 } 1568 } (A_1+E) 1552 }	1194+373=1567 or J-T 1280+276=1556 or J-T
	1430(b_2)	C=O + CH bend		1523(e, a_2)	1280+276=1556; 1281+277=1558 or J-T
	1390(b_1)	CH ₃ deg.def.		1430(e, a_2)	C=C-C 77 %
	1284(a_1)	C=C + C-CH ₃ str.		1390(e, a_2)	CH ₃ deg.def.
				1284(e)	C=O same

of C=C bond because of the uneven distribution of electron clouds in C=O. Bayliss' results⁶ support this assumption.

(iv) The polymeric bands and Jahn-Teller splitting disappear in dilute solutions.

Using assumption (iii) and from tables of solvent shifts (Table 2-11) the bands near 1590 and 1400 cm^{-1} are assigned as C=O stretching symmetric and asymmetric respectively. The bands near 1530 and 1270 cm^{-1} are assigned as C=C-C stretching asymmetric and symmetric respectively. This is true for all M(II) and M(III) except Pd(II). The discussion of Pd(II) anomaly will follow shortly. Using assumptions (i), (ii); and (iv), fundamentals, polymeric species, combinations/overtones and Jahn-Teller splittings are thus assigned (Tables 12 and 13, last column). Also, symmetry species of the observed frequencies are noted. M(II) chelates are assumed to have a molecular symmetry of $\sim C_{29}$ and M(III) chelates $\sim D_3$. All these assignments are tabulated in Tables 12 and 13 together with other assignments. It can be seen that the present results on fundamental frequencies agree with those assigned by isotopic substitution methods and contrary to those assigned by normal co-ordinate treatment. There is little doubt that the latter assignments are wrong because of the necessary assumptions made in normal co-ordinate calculations.

3.3 The Pd(II) Anomaly

This compound does not follow the usual solvent shift patterns of the other chelates. Perhaps this is due to its different structure.¹⁴

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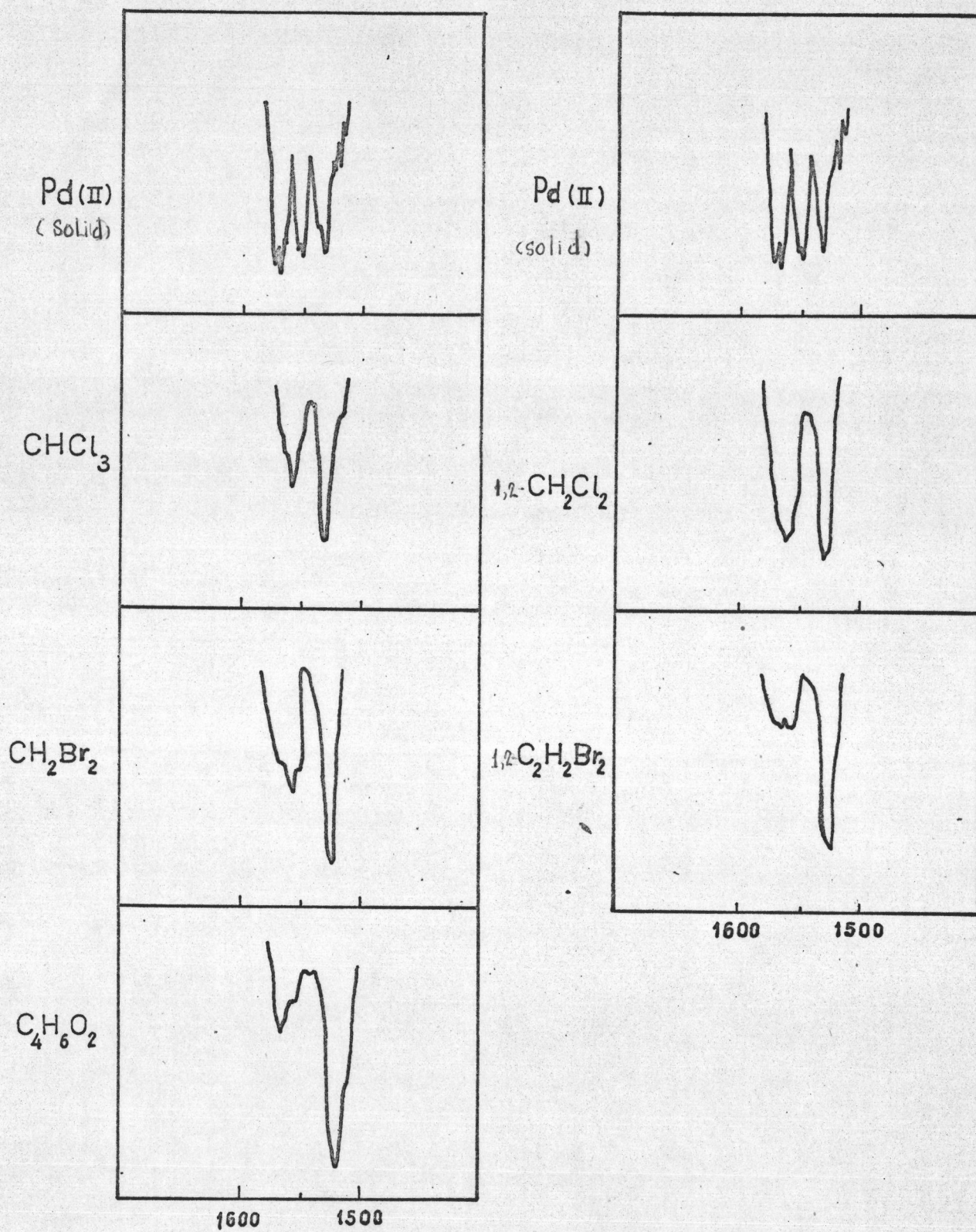


Fig. 7 Fermi resonance in Pd(II) acetylacetonate.

From the $\Delta\nu$'s measurement (Table 3) the 1531 cm^{-1} band should be assigned as C=O and 1550 cm^{-1} as C=C=C. This is contrary to the ^{18}O isotopic substitution work by Musso and his co-workers²⁷ and indeed, all the rest of the M(II) and M(III) acetylacetonates.

In order to reconcile with Musso's results it is necessary to look for some other explanations. Fermi resonance seems to be the answer, i.e. a fundamental frequency is in resonance with a combination band (or overtone.) provided that they belong to the same symmetry species. Thus the 2 bands acquire characteristics of both: part fundamental and part combination band. This results in increase in intensities of both bands, each borrowing from one another.

Fig. 7* supports the occurrence of Fermi resonance. In five solvents, the 1531 cm^{-1} (b_2) band has shifted towards $\sim 1523\text{ cm}^{-1}$ and this is in Fermi resonance with 1518 cm^{-1} (solid) = $1278+263 = 1543\text{ cm}^{-1}$ (B_2). Hence the appreciable increase in intensity of this shifted band at $\sim 1523\text{ cm}^{-1}$ Musso's work²⁷ in CHCl_3 shows the same increase in intensity (1520 cm^{-1}) If the 1518 cm^{-1} (shoulder) were polymeric species, then this band would disappear in dilute solutions (due to preponderance of monomers) making the 1523 cm^{-1} band less intense relation to the 1568 , 1550 cm^{-1} bands

When Fermi resonance is taken into account we can average the 1531 and 1518 bands, i.e. 1526 cm^{-1} (see Table 3), and the resultant $|\Delta\nu| = 3.3\text{ cm}^{-1}$ in contrast to the 1550 cm^{-1} band's

$|\Delta\nu| = 4.4$, i.e. 1550 cm^{-1} is now C=O stretch and 1531 is

* In CH_2Cl_2 , the 1560 cm^{-1} band is partly solvent.

C=C-C- stretch in agreement with assumption (iii).

3.4 Fermi Resonance and Jahn-Teller Splitting in M(III)

Combination bands are listed, together with their symmetry species in the last two columns in Table 13.

For example in Cr(III), 1578, 1568 and 1554 cm^{-1} can be assigned as combination bands of symmetry ($A_1 + E$). If they are indeed combination bands, then Fermi resonance is possible, i.e. in Cr(III); 1582 cm^{-1} (fundamental band) in Fermi resonance with the 1578 and or 1568 cm^{-1} bands, and 1535 cm^{-1} (fundamental band) in Fermi resonance with 1554 cm^{-1} . Similarly for all other M(III) chelates.

Another interpretation of these weaker bands in solids (Fig. 3) is of course Jahn-Teller effects already mentioned. The molecular symmetry D_3 can be distorted by its surroundings to C_2 . In so doing, numerous bands can appear:-

D_3		C_2	
A_1	Raman	A	
A_2	inactive	B	all I.R. active
E	I.R. and Raman	A+B	

Typical solvent shift spectra (Fig. 6) show that in dilute solutions, Jahn-Teller splitting begins to disappear. The Jahn-Teller effect is being removed: $C_2 \rightarrow D_3$, the molecular structure $\sim D_3$ of M(III) is leaving the crystal site C_2 .

It is very difficult to distinguish Fermi resonance from Jahn-Teller splitting because the frequency separations of these weaker bands from the fundamentals are very small $\sim 10 \text{ cm}^{-1}$. Usually Fermi resonance frequency separations are in the order

of 100 cm^{-1} plus.

3.5 Polymeric Species, Overtones and Combination Bands in M(III)

Again, it is very difficult if not impossible to distinguish between polymeric species bands and overtones/combination bands. Since polymeric species exist in M(II), the weaker bands are assigned as such in preference. Obviously, overtones and combination bands cannot be ruled out. For example, Table 12, Co(II), the 1518 cm^{-1} band could be a combination of $1264+258 = 1522 \text{ cm}^{-1} (\text{B}_2)$. 258 cm^{-1} is calculated by Nakamoto et al.²¹ There are numerous other possibilities as in M(III), Table 13.

In dilute solution, monomeric species become dominant as already mentioned (Fig. 4)

3.6 Electron Delocalization of Chelate Ring

From Table 2-11 it can be seen that both C=O and C=C=C bonds show solvent shifts, $\Delta\nu$. When necessary, the absolute values are taken and averaged: $\sum \frac{|\Delta\nu|}{n}$, because negative signs are believed to be unimportant for comparing magnitudes of the shifts. This is interpreted to mean that there is appreciable mixing of the two vibrational modes. This is a well known phenomenon and is very wide spread in vibrational spectroscopy. The percent of mixing calculated is based on

$$\frac{\Delta\nu_{\text{C=O}}}{\Delta\nu_{\text{C=O}} + \Delta\nu_{\text{C=C=C}}} \times 100$$

These are also tabulated in Tables 12-13.

The percentage figures are not to be taken literally. But they do indicate appreciable mixing, for example, as calculated by normal co-ordinate treatments.^{21,28,33} This means delocalization of π electrons around the ring.

Results from isotopic substitution methods showed similar effects. Using O^{18} in Cu(II) the 1578 cm^{-1} band shifts,²⁷ $\Delta\nu = -26\text{ cm}^{-1}$ and 1527 cm^{-1} band shift, $\Delta\nu = -5\text{ cm}^{-1}$. This is due to the mixing of modes.

Finally from X-ray work of many acetylacetonate chelates²⁷ C=O bonds are equal (average 1.27 \AA) and C-C bonds are also equal (average 1.39 \AA). They indicate a bond and a half, i.e. delocalization of π electron around the ring.

3.7 Solvent Shifts of C=O and M-O Bond Strengths in M(II) and M(III)

There is a definite correlation between solvent shifts $\frac{|\Delta\nu|}{\nu_{\text{solid}}}$ of C=O and Urey-Bradley stretching force constants of M-O bonds³¹ (Figs. 8A, 8B).

The Pd(II) (Fig. 8A) is off the straight line, this could be due to its different crystal structure from the others.¹⁴

Urey-Bradley force constant (K) of Mn-O bond has not been calculated. From our plots (Fig. 8A and 8B) we can predict the force constants of Mn(II) and Mn(III) being equal to $1.20-1.35$ and $1.45-1.85 \times 10^5$ dyne. cm^{-1} , respectively, knowing $\frac{|\Delta\nu|}{\nu_{\text{solid}}}$

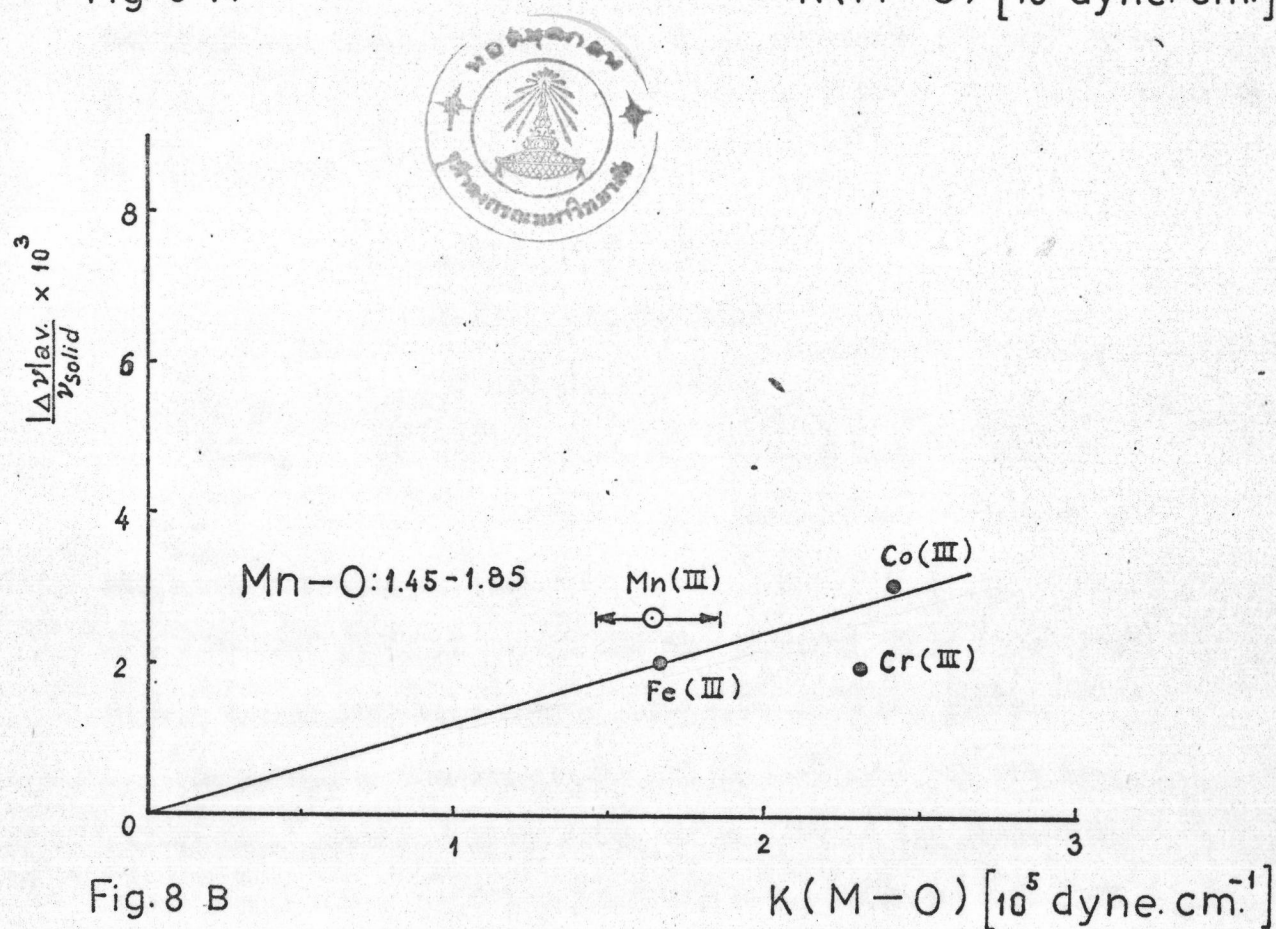
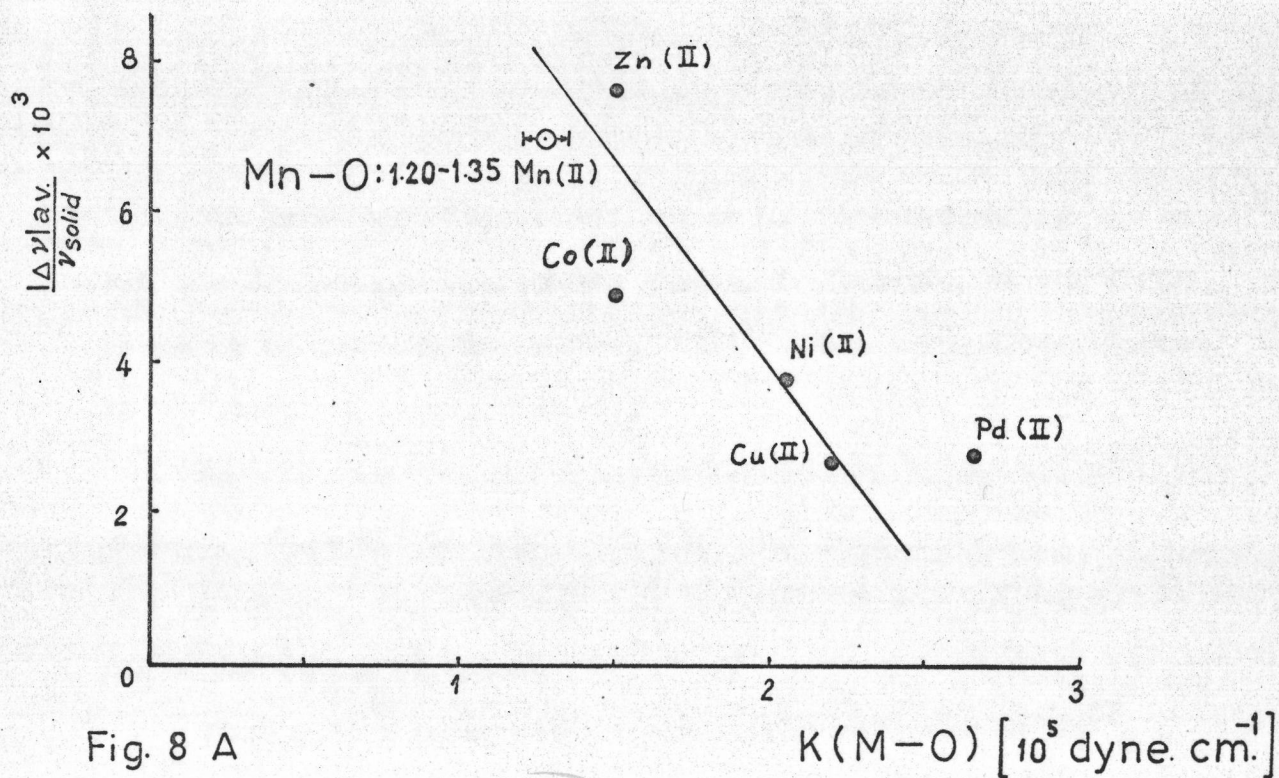


Fig. 8 Plot of the average of solvent shifts of $C\equiv O$ str. band vs. force constant K_{M-O} of metal acetylacetonate.

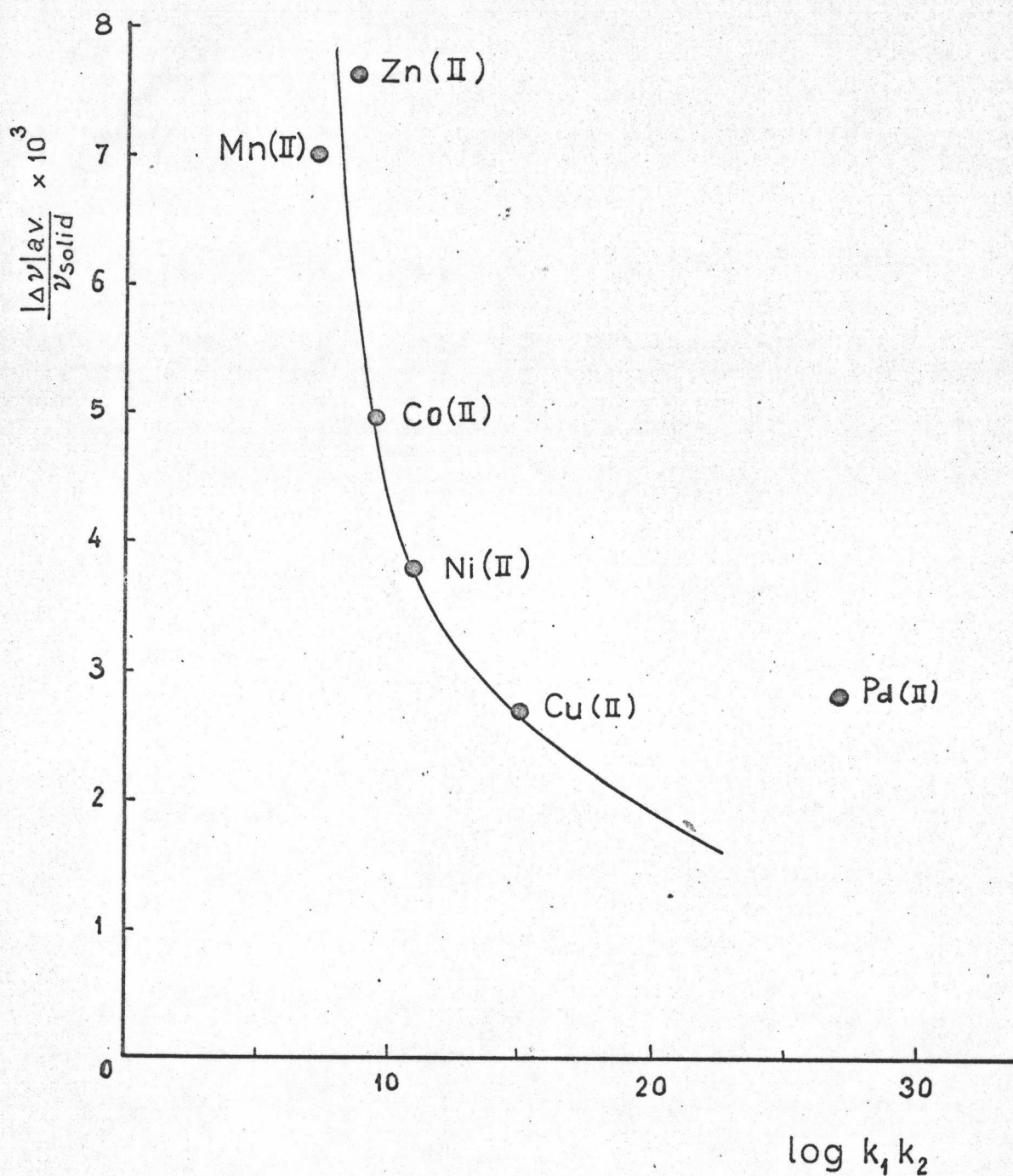


Fig. 9 Plot of the average of solvent shifts of C \equiv O str. band vs. log of stability constants of M(II) acetylacetonate.

from Tables 7 and 9. The force constants are reasonable figures.

Also the same correlation occurs when $\frac{|\Delta\nu|}{\nu_{\text{solid}}}$ of C=O

is plotted against $\log k_1 k_2$ where k's are stability constants. Once again Pd(II) is off the ~~s~~ curve (Fig. 9).

Furthermore (Tables 2-7), Co(II), Mn(II), and Zn(II) show big solvent shifts, 7.8, 11.3 and 12.3 respectively, indicating that C = O bonds are more "free" which in turn suggest that Zn(II), Mn(II), and Co(II) form weaker bonds with oxygen atoms. By the same reason, Cu(II) and Pd(II) are strong chelates, with shifts of 4.3 and 4.4 respectively (Tables 2 and 3). This can be represented by Fig. 10.

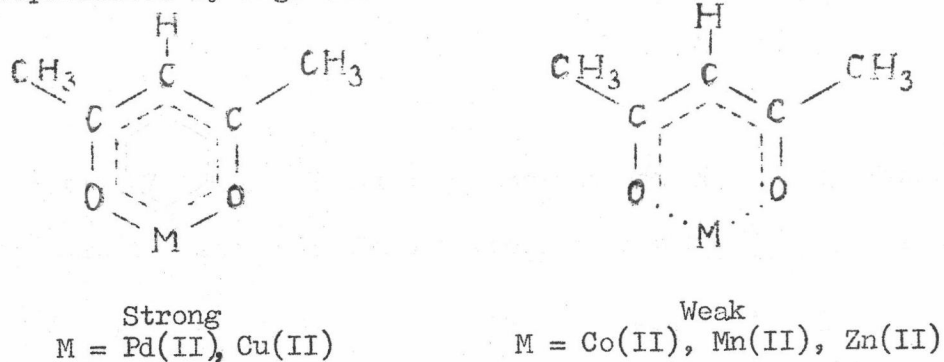


Fig. 10 Strengths of M(II) chelates

The correlation is not as good for M(III) (Fig. 8B).

The reason could well be that the Nakamoto et al³³ assignments of M-O stretch are wrong, as suggested by O¹⁸ substitutions of Cr(III) and Mn(III) acetylacetonates.²⁶

3.8 Conclusion

The solvent shift studies here do show important indications on the bond properties of solutes and solute-solvent interactions. Namely, the assignments of fundamentals; the possibilities of combination bands, of Fermi resonance; the disappearance of polymeric species in dilution of M(II), likewise the removal of splitting in M(III). Further, we have established the correlation between the magnitudes of the C=O solvent shifts and that of M-O bond strengths and also the delocalization of π electrons around the chelate rings.

It would be interesting to apply solvent effects to the M-O stretching vibrations of M(II) and M(III) acetylacetonates. Unfortunately, their vibrations are in the far infrared regions.

Perhaps, it is now appropriate to comment on the general situation of solvent effects. The constants C's in equations(II)-(V) are adjustable parameters, therefore, they can be made to draw straight lines. Furthermore, these parameters have little physical meaning, other than vague terms like: electrical properties, specific interactions, or inductive terms.

There is no doubt that solvent effects are complicated with all factors, dipole moments μ , dielectric constants ϵ , refractive indices n , polarizabilities, α , size, structure, orientations of molecules, dispersion forces, ... come into play. It is doubtful that there will ever be a satisfactory unified

theory to explain solvent effects.

The Bellamy plot (equation V) is an alternate approach to the study of solvent shifts. It essentially eliminates the problem of solvent properties, because it is a plot between solutes and a reference solute. This seems to defeat its expressed purpose to study solvent effects. It would be more accurate to call the Bellamy plots "solute effects". Further, the slopes straight line plots depend solely on the choice of the reference solute. For C=O shifts, acetophenone is used as a reference and for N-H, pyrrole is used. These compounds are chosen for no particular reasons, other than to produce the best straight lines.

However, the above difficulties should not deter further investigations in the general area of solvent effects.

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