It was noted that γ-basic lead azide I yielded absorption features for the azide grouping and for lead-oxygen bonding only. There was no evidence whatsoever for absorption due to the hydrogen-oxygen bond so that complete absence of hydroxyl ion and water of crystallisation must be concluded.

The results of this work indicate that γ-basic lead azide I is an oxyazide which does not conform to the formulation $Pb(N_3)_2 \cdot PbO$. Such a formula should yield analytical figures for lead and nitrogen of 80.6% and 16.3% and although the lower analytical figures for our two preparations could indicate an impure product, a complex of approximate formula $Pb(N_3)_{0.96}\,O_{0.66}$ is considered likely.

Results to date indicate that in any assessment of the purity of a γ-basic lead azide I sample by chemical methods, the lead and azide figures should be at least 80.3% and 15.6%, respectively. Frequent impurities are basic lead carbonate and normal lead azide. It is worth noting that the presence of basic carbonate will lower the azide figure without affecting the lead figure substantially whereas the presence of normal azide will lower the lead figure and raise the azide figure. The return of an acceptable azide figure but a low lead figure may indicate the presence of both basic lead carbonate and normal lead azide as impurity.

The authors wish to thank members of the staff of ERDE and RARDE for the supply and chemical analysis of samples of basic lead azide.

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244. Infrared Spectra of α-Thenoyl-trifluoroacetonates of Metal Ions of the First Transition Series

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(14. V. 71)

Summary. The IR. spectra of α-thenoyl-trifluoroacetone (HTTA) and seventeen of its chelates with metal(II) and -(III) ions of the first transition series have been determined. Three series of complexes are represented: the anhydrous metal(II) species, $[M(TTA)_2]_n$ (M = Ca, Mn, Co, Ni, Cu, Zn); metal(II) dihydrates, $[M(TTA)_2(H_2O)_2]$ (M = Mn, Fe, Co, Ni, Zn); and the metal(III) chelates, $[M(TTA)_3]$ (M = Sc, V, Cr, Mn, Fe, Ga). For each metal(II) complex, the spectra of the anhydrous and hydrated compounds are practically identical, suggesting that the anhydrous complexes have the polynuclear octahedral structure established for the corresponding acetylacetonates. Magnetic moment determinations reveal that complexes of the $3d^4$–$3d^7$ ions all have

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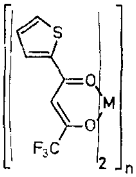
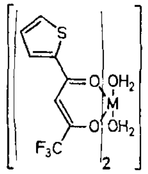
[1] On leave during 1971 for study at the Laboratorium für anorganische Chemie, Eidg. Technische Hochschule Zürich.

spin-free configuration. Several vibrational bands with frequencies <700 cm^{-1} are found to exhibit a frequency variation with *d*-orbital population which is consistent with the order of crystal field stabilization energies and hence with their assignment as coupled metal-oxygen stretching modes. Unique features of the spectra of $[Cu(TTA)_2]$ and $[Mn(TTA)_3]$ are ascribed to structural differences arising from *Jahn-Teller* distortion. Tentative assignments for the majority of the ligand vibrations are given.

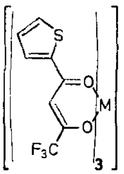
Introduction. – The majority of reports on metal α-thenoyl-trifluoroacetonates relate to their rôle as synergists in the solvent extraction of metal ions by phosphorus esters [1] [2]. Although many of the complexes have been isolated, no systematic study of their spectroscopic properties has been reported. Here we report on the IR. spectra of all the preparatively-accessible TTA-complexes I, II and III of the metal(II) and -(III) ions of the first transition series.



(I)



(II)



(III)

Experimental. – The complexes were prepared by the general method previously reported [3] except that either the metal acetate, chloride or nitrate, buffered with sodium acetate, was employed. Adjustment of the pH of the solution to 6 is necessary for precipitation of the Ca^{II}, Sc^{III} and Ga^{III} complexes. This method yields the dihydrates of the metal(II) complexes except for those of Ca^{II} and Cu^{II}, obtained only in the anhydrous form. Dehydration of the Mn^{II}, Co^{II} and Zn^{II} complexes is accomplished within 3 h at 110°/0.2 Torr, that of the Ni^{II} complex requires 5 h at 180° at this pressure. The Mn^{III} complex was prepared from Mn^{III} acetate by an analogous procedure to that described for the tropolonate [4]. The V^{III} complex is very susceptible to oxidation and was prepared and handled throughout under dry nitrogen. The Ca^{II}, Sc^{III}, V^{III}, Mn^{III} and Ga^{III} complexes are believed to be reported for the first time.

IR. spectra were determined on a *Beckman* IR-12 spectrophotometer calibrated against carbon dioxide and water vapour. Samples were in the form of Nujol mulls between caesium bromide or (below 350 cm^{-1}) caesium iodide plates. For maximum precision, frequencies were read from the wave-number drum, not the chart paper. Replicate spectra yielded a maximum discrepancy of 1 cm^{-1} below and 2 cm^{-1} above 1000 cm^{-1}. Magnetic moments were determined on a *Newport-Stanton Gouy* balance.

Results and Discussion. – The IR. spectra of the α-thenoyl-trifluoroacetonate complexes are depicted in Figs. 1 and 2 and the frequencies listed in Table 1. No crystallographic studies have been made on these complexes. Like their acetylacetonate analogues, the metal(II) derivatives are isolated as the dihydrates except for the Ca^{II} and Cu^{II} compounds. *Trans*-octahedral conformation has been established [5] for the acetylacetonate dihydrates and is presumed for the α-thenoyl-trifluoroacetonate dihydrates. Certainly, none of the complexes $[M(TTA)_2(H_2O)_2]$ exhibits any spectral differences which could be ascribed to isomerism and their spectral band patterns are practically identical with those of the octahedral $[M(TTA)_3]$ compounds.

Dehydration of the dihydrates is readily effected by moderate heating under reduced pressure, except for the thermolabile Fe^{II} complex dihydrate. The anhydrous complexes (except for that of copper) yield spectra which are practically identical (with respect to band frequencies and intensities) with those of the dihydrates. This suggests that they are analogous with the anhydrous metal(II) acetylacetonates [5] in being correctly formulated as polynuclear octahedral species, $[M(TTA)_2]_n$, $n > 1$, already shown for $[Ni(TTA)_2]$ by its electronic spectrum [2]. Even $[Ca(TTA)_2]$ yields an IR. spectrum consistent with this structure and there is evidence [6] that other Ca^{II} β-keto-enolates are probably not tetrahedral monomers and the Ca^{II} ion is known [7] to form the octahedral species $K[Ca(acetylacetonate)_3]$ [6]. The spectrum of the Cu^{II} complex exhibits some features which indicate that it probably has the square planar configuration established [5] for Cu^{II} acetylacetonate, *viz.* a unique strong band at 556 cm^{-1}, splitting of the ligand band near 530 cm^{-1} and reversal of the relative intensities of the two bands near 1600 cm^{-1}.

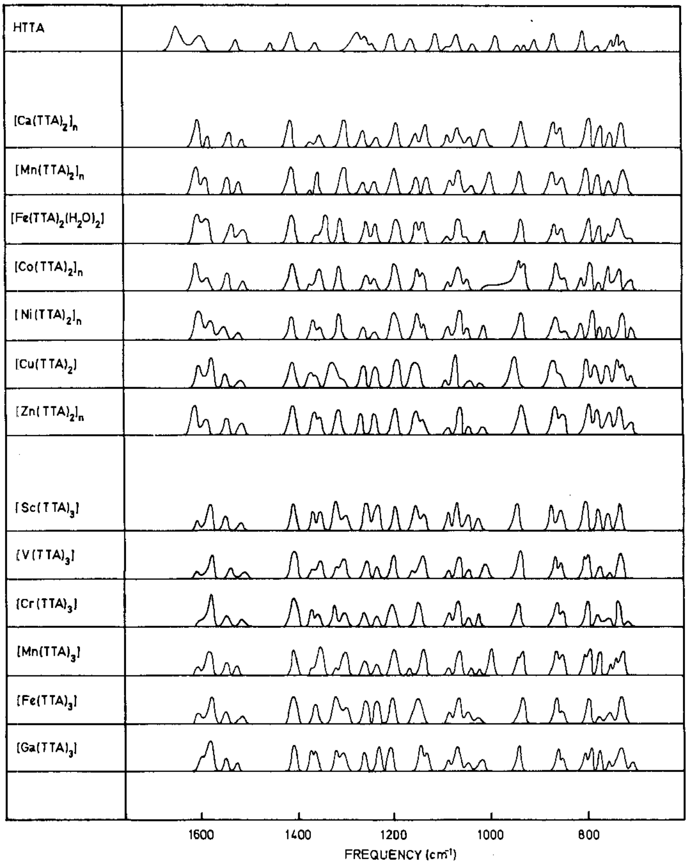


Fig. 1. *Infrared spectra of thenoyltrifluoroacetone complexes, 1600–700 cm^{-1}*

The far IR. spectra of the anhydrous and hydrated metal(II) complexes reveal that four bands exhibit significant sensitivity to the nature of the co-ordinated metal ion and would, on this basis alone [7], be assigned to more or less pure M–O stretching vibrations. Although metal-ion sensitivity has frequently been used to assign metal-ligand vibrations, we have recently shown [8] that in a series of isostructural complexes of first transition series ions, the shift in $\nu M{-}L$ follows the order of crystal field

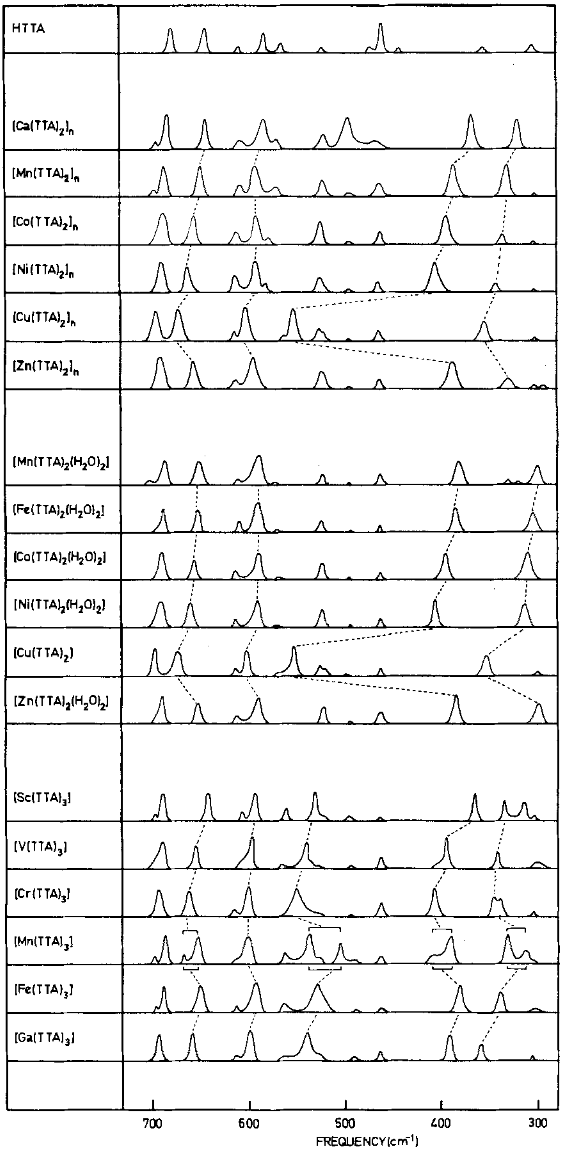


Fig. 2. *Infrared spectra of thenoyltrifluoroacetone complexes, 700–300 cm*$^{-1}$

stabilization energies (CFSE.'s), for which those pertaining to the complexes studied here are given in Table 2. These have been derived from the known relationships [9]

$$\text{CFSE.} = -(4\,n_t - 6\,n_e)\,Dq \tag{1}$$

$$\text{and}\quad 10\,Dq = fg \tag{2}$$

$$\text{whence}\quad \text{CFSE.} = -(0.4\,n_t - 0.6\,n_e)\,fg, \tag{3}$$

Table 1. *Vibrational frequencies of metal α-thenoyl-trifluoroacetonates* (cm^{-1})

$[M(TTA)_2]_n$						$[M(TTA)_2(H_2O)_2]$					$[M(TTA)_3]$						Assignment
Ca	Mn	Co	Ni	Cu	Zn	Mn	Fe	Co	Ni	Zn	Sc	V	Cr	Mn	Fe	Ga	
1603	1609	1607	1606	1600	1611	1610	1603	1608	1608	1610	1603	1604	1600	1603	1602	1592	νC—O
1584	1594	1585	1579	1578	1585	1586	1583	1584	1584	1585	1584	1575	1579	1585	1580	1583	νC—C
1544	1542	1548	1548	1548	1551	1541	1540	1544	1548	1541	1550	1541	1549	1547	1550	1553	thienyl ring stretch
1516	1519	1509	1519	1514	1516	1515	1508	1512	1509	1516	1517	1508	1515	1524	1517	1526	
1414	1412	1415	1414	1409	1413	1413	1415	1414	1415	1414	1411	1409	1410	1406	1411	1410	
1369	1369	1368	1365	1364	1360	1358	1359	1360	1360	1359	1363	1367	1363	1369	1362	1368	
1353	1357	1355	1352	1358	1352	1351	1353	1351	1354	1353	1354	1355	1354	1354		1358	
1302	1301	1310	1310	1328	1310	1306	1310	1313	1312	1312	1319	1319	1323	1319	1320	1320	
				1299							1297	1304	1300	1299	1298	1303	νC—C + νC—R
1257	1259	1255	1259	1263	1261	1260	1258	1261	1260	1263	1258	1258	1260	1260	1258	1263	
1235	1236	1236	1235	1236	1236	1236	1236	1236	1237	1236	1235	1235	1236	1235	1235	1236	νC—F
1195	1194	1196	1195	1190	1196	1194	1195	1194	1196	1196	1197	1203	1203	1200	1202	1203	
1150	1150	1151	1149	1155	1152	1152	1149	1150	1152	1150	1151	1160	1150	1165	1149	1146	δC—H in-plane
1132	1130	1139	1139		1135	1133	1140	1132	1133	1130	1135	1140		1140		1133	
1084	1082	1085	1084	1087	1085	1085	1085	1085	1085	1087	1084	1088	1086	1087	1085	1086	δC—H in-plane thienyl
1063	1064	1065	1065	1069	1065	1066	1064	1065	1065	1065	1068	1067	1070	1067	1068	1070	
1038	1036	1043	1044	1038	1041	1038	1044	1040	1045	1045	1042	1042	1043	1035	1042	1043	δC—H in-plane thienyl
1010	1000	1011	1012	1020	1010	1011	1010	1009	1011	1010	1022	1013	1021	1013[a]	1019	1019	
935	938	933[b]	938	943	935	935	936	935	937	934	940	937	940	936[c]	938	939	δC—H out-of-plane thienyl
865	871	862	864	866	863	864	862	862	862	862	868	862	864	862	864	864	
851	845	845	840	852	851	852	850	851	850	851	850	850	850	850	850	852	C—CF_3
794	800	802[d]	802[e]	798	793	794	794	793	791	793	800	801	797	799[f]	797	797[g]	δC—H out-of-plane thienyl
770	773	774	775	779	775	774	773	774	776	774	773	774	778	774	776	775	δC—H out-of-plane chelate
752	755	750	753	756	752	752	754	752	752	752	755	753	754	754	755	754	νC—CF_3
727	723	728	724	726[h]	729	724	729	729	729	729	729	731	728	736[i]	725	729	
697	696	703	707	708	704	701	701	703	706	702	696	697	705	697	696	704	CF_3
686	689	689	689	698	691	689	689	690	691	689	690	690	694	687	691	690	

Table 1 (continued)

$[M(TTA)_2]_n$						$[M(TTA)_2(H_2O)_2]$					$[M(TTA)_3]$						Assignment
Ca	Mn	Co	Ni	Cu	Zn	Mn	Fe	Co	Ni	Zn	Sc	V	Cr	Mn	Fe	Ga	
646	650	657	664	675	659	653	654	658	663	655	645	657	665	667	652	660	$(\nu M—O)_1$
														653			$\nu Mn—O$
610	610	614	616	616	615	612	612	615	616	614	609	613	620		611	615	chelate ring def.
585	591	591	592	604	596	590	591	591	591	591	595	597	602	601	593	595	$(\nu M—O)_2$
562	563	565	569	563	560	570	566	563	563	562	563	568	565	565	565	564	CF_3
				531							533	540	552	539	530	540	$(\nu M—O)_3$
521	525	525	523	522	523	523	525	522	523	521	520	530	520	525	520	523	CF_3
														505			$\nu Mn—O$
496	495	495	495	495	495	500	500	495		490	495	495	495	495	495	490	CF_3
470	462	465	465	463	463	465	465	464	465	462	465	464	465	464	465	464	thienyl
369	387	396	403	556	389	382	386	395	407	384	367	396	408	410	381	393	$(\nu M—O)_4$
														389			$\nu Mn—O$
319	328	335	342	356	330	300	305	311	314	300	334	344	346	331	340	357	$(\nu M—O)_5$
														312			$\nu Mn—O$
													337				

Mean of doublet at: [a]) 1023 and 1003, [b]) 935 and 930, [c]) 939 and 933, [d]) 811 and 792, [e]) 814 and 790, [f]) 803 and 795, [g]) 802 and 794, [h]) 731 and 720, [i]) 740 and 732 cm^{-1}

Table 2. *Analytical, magnetic moment and CFSE. data on metal α-thenoyl-trifluoroacetonates*

M	Con-figur-ation	Calculated %C	Calculated %H	Found %C	Found %H	μeff (289K) B.M.	g kK	Crystal field stabilization energy Dq	f	kK[a]	$(\nu-\nu_0)$ $(\nu$M—O$)_1$ cm^{-1}	$(\nu$M—O$)_4$ cm^{-1}
$[M(TTA)_2]_n$												
Ca	d^0	39.8	1.7	39.9	1.8	–	–	0	0	0	0	0
Mn	d^5	38.6	1.6	38.3	1.5	5.51	8.5	0	0	0	0	0
Co	d^7	38.3	1.6	38.0	1.5	4.99	9.3	8	7.44	8.93	4	8
Ni	d^8	38.4	1.6	38.0	1.7	–	8.9	12	10.68	12.82	9	15
Cu	d^9	38.0	1.6	38.0	1.8	–	12.0	6	7.20	8.64	18	167
Zn	d^{10}	37.9	1.6	37.7	1.5	–	–	0	0	0	0	0
$[M(TTA)_2(H_2O)_2]$												
Mn	d^5	36.0	2.3	35.2	2.2	5.94	8.5	0	0	0	0	0
Fe	d^6	36.0	2.3	35.0	2.4	5.30	10.0	4	4.00	4.80	1	4
Co	d^7	35.8	2.3	35.9	2.4	4.86	9.3	8	7.44	8.93	4	12
Ni	d^8	35.8	2.3	36.1	2.6	–	8.9	12	10.68	12.82	9	24
Zn	d^{10}	35.3	2.2	35.4	2.1	–	–	0	0	0	0	0
$[M(TTA)_3]$												
Sc	d^0	40.7	1.7	41.0	2.1	–	–	0	0	0	0	0
V	d^2	40.4	1.7	40.6	1.8	–	18.6	8	14.88	17.86	9	24
Cr	d^3	40.3	1.7	41.1	2.1	–	17.0	12	20.40	24.48	16	33
Mn	d^4	40.1	1.7	40.1	1.8	6.16	21.0	6	12.60	15.12	9[b]	21[c]
Fe	d^5	40.1	1.7	39.2	1.9	5.89	14.0	0	0	0	0	0
Ga	d^{10}	39.3	1.7	39.1	1.7	–	–	0	0	0	0	0

[a] Assuming $f(\text{TTA})_3 = f(\text{acetylacetonate})_3 = 1.2$ [9].

[b] νMn—O taken as mean of bands at 667 and 653 cm^{-1}.

[c] νMn—O taken as mean of bands at 410 and 389 cm^{-1}.

where n_t and n_e are the numbers of t_{2g} and e_g electrons and eq. (2) represents *Jørgensen's* factorization of the crystal field parameter 10 Dq into its metal ion (g) and ligand (f) components. Using available [9] values of g, the CFSE.'s may be calculated in terms of f which is a constant for each of the three series of complexes studied. A prerequisite to calculation of the CFSE.'s is a knowledge of the spin states of the d^4-d^7 ions in the complexes. The room temperature magnetic moments (Table 2) reveal that they all have high spin configuration, in common with the corresponding acetylacetonates [10].

The band exhibiting maximum metal sensitivity (and therefore assigned as the least-coupled νM–O) is the intense band near 400 cm^{-1}, a region where the free ligand, HTTA, does not absorb. The variation of the frequency of this band with d-orbital population is shown in Fig. 3. The frequencies for the complexes of ions with zero CFSE., *viz.* those of the d^0, spin-free d^5 and d^{10} ions, Ca^{II}, Mn^{II} and Zn^{II}, form an interpolation line which is used to estimate the frequencies (ν_0) which would be realized in the absence of crystal field stabilization. The difference between ν_0 and the observed frequencies (ν) therefore represents that part of νM–O which is attributable to the CFSE. The values of $(\nu - \nu_0)$ correlate very well with the CFSE. values

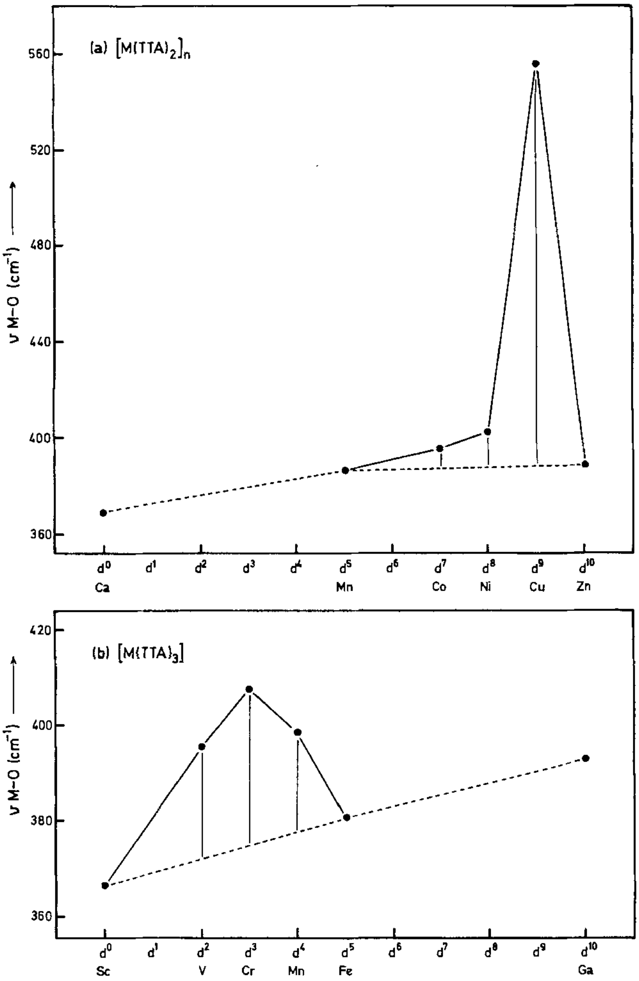


Fig. 3. *Relationship between frequency and* d-*orbital population for the most sensitive νM—O band,* $(\nu M\text{—}O)_4$

The dashed line is the interpolation line and the vertical lines represent $(\nu - \nu_0)$. The point for Mn^{III} is taken as the mean of the bands at 410 and 389 cm^{-1}.

except for the Cu^{II} complex (Table 2). Precisely similar conclusions pertain to the dihydrates and generally to the less-sensitive metal-ligand bands.

Of the unique features in the spectrum of the Cu^{II} complex, the most striking is the strong band at 556 cm^{-1}, which clearly (Fig. 2) corresponds with those near 400 cm^{-1} in the spectra of the other complexes. The abnormally high νCu–O value is not unexpected if the Cu^{II} complex is the only 4-co-ordinate complex of the series since the bonding capacity is distributed over four bonds rather than six. A similar situation exists [11] for the complexes: tetrahedral monomeric [CoCl$_2$py$_2$] (νCo–N = 252 cm^{-1}) and octahedral polymeric [CoCl$_2$py$_2$]$_n$ (νCo–N = 224 cm^{-1}). The high νCu–O value is also expected on theoretical grounds since, of the metal(II) ions studied, only Cu^{II} is subject to strong *Jahn-Teller* distortion. The extra stabilization arising from this distortion is not included in the CFSE. given in Table 2.

The spectra of the $[M(TTA)_3]$ complexes reveal five significantly metal-sensitive bands. The values of $(\nu - \nu_0)$ again exhibit a well-defined correlation with the CFSE.'s. The unique character of the spectrum of the spin-free d^4 Mn^{III} complex is apparent from Fig. 2 and is distinguished by a splitting of the metal-sensitive bands. Of the trivalent ions studied, Mn^{III} is the only one for which strong *Jahn-Teller* distortion is expected. Crystallographic studies of Mn^{III} acetylacetonate reveal tetragonal structure although the static distortion is very small [4] [12]. Assuming similar distortion in $[Mn(TTA)_3]$, splitting of the νMn–O bands is a logical result of the existence of short and long Mn–O bond lengths. The mean value of νMn–O for each metal-sensitive band is usually in the order expected from the CFSE.'s: Cr > Mn > Fe.

In the complexes of ions with zero CFSE., the νM–O values generally exhibit an increase in the order Ca < Mn < Zn and Sc < Fe < Ga. This is consistent with the expected effect on the frequencies of the ionic radius contraction through the series but is the opposite of that expected from the relative ionic masses. Clearly the former outweighs the latter in determining the frequency order. Since the variation in ionic mass for the transition series ions is relatively small, the contribution of the mass effect to the frequencies is insignificant.

In Table 1, tentative vibrational assignments, for bands other than metal-ligand vibrations, have been made with the aid of the extensive theoretical and empirical studies on the IR. spectra of metal β-keto-enolates. Electron delocalization in the chelate ring leads to extensive coupling so that few bands represent pure vibrations. Earlier empirical assignments [13] of the first two bands below 1700 cm^{-1} in metal acetylacetonates to (predominately) νC—O and νC—C respectively, were reversed [14] by a normal co-ordinate treatment of the Cu^{II} complex, but subsequently supported by a more refined treatment [15] and by ^{18}O-labelling of the carbonyl oxygen [16]. In phenyl-substituted β-keto-enolates a third band appears near 1600 cm^{-1}, which has been ascribed [17] to the first aromatic ring stretching vibration, since it is insensitive to the nature of the co-ordinated ion and its frequency is close to that observed for monosubstituted benzenes. The first heterocyclic ring stretching vibration is at a much lower frequency (1523 ± 9 cm^{-1} [18] [19]) and bands are observed in this region in the spectra of HTTA and its complexes. Unlike phenyl-substituted β-keto-enolates, there are therefore no complications from overlap of these bands with νC—O and νC—C and the assignment is comparatively straightforward. Further thienyl ring stretching vibrations occur at 1442 ± 12 and 1354 ± 7 cm^{-1} and thienyl C—H deformation frequencies are at 1081 ± 3, 1043 ± 7, 925 ± 8, 853 ± 7 and 800 cm^{-1} [18]. Bands near all of these frequencies are observed in the spectra of HTTA and its chelates. Vibrational bands originating in the CF_3-group are assigned by comparison with the spectrum of CF_4 [20] and normal coordinate studies of tri- and hexa-fluoroacetylacetonates [21].

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245. Spectroscopic Evidence for Symmetry-Restricted π-Interaction in Vanadyl β-Keto-enolates

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Summary. Theoretical treatments of the distorted square pyramidal co-ordination observed in vanadyl β-keto-enolates predict restricted interligand conjugation and minimal π-interaction in the oxovanadium-ligand bonds. The effects of ligand substitution on the vibrational and electronic spectra of vanadyl β-keto-enolates yield evidence that strong σ-bonding and ionic contributions are chiefly responsible for the strong vanadium-ligand bonding.

Introduction. – Elsewhere [1] we were able to achieve a qualitative separation of the relative contributions of metal-ligand (M → L) and ligand-metal (L → M) π-interaction in transition metal(III) β-keto-enolates by examination of the electronic, IR. and NMR. spectroscopic data from these octahedral complexes, in which the metal d_ε orbitals have full π-function. Vanadyl β-keto-enolates have distorted square pyramidal structure I, the vanadium atom being displaced from the basal plane of the four β-keto-enolate oxygen atoms towards the apical multiply-bonded oxygen atom [2] [3] [4]. Compared with regular square pyramidal structure, this distortion leads to some loss of π-function by the vanadyl $d\pi$ orbitals (d_{xz}, d_{yz}) and severely restricted interligand conjugation [5]. The latter implies a considerable limitation in the capacity of the substituents for resonance interaction with the V–O and V=O bonds. Quite apart from such symmetry constraints to π-interaction,

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