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Spectra and Bonding of Diethyldithiocarbamate Complexes. III. The Electronic Spectra of Complexes of Trivalent Open-Shell Central Atoms

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The electronic spectra of tris(diethyldithiocarbamato) complexes of central atoms with open-shell configurations are discussed in terms of central atom (d–d) and electron transfer transitions. The splitting and the electronic repulsion parameters obtained from the d–d spectra are used to calculate the energies of the charge transfer bands using a method described by Jørgensen. It is shown that the complexes of Cr^{III}, Fe^{III}, Rh^{III}, and Ru^{III} are nearly octahedral, while for Mn^{III}, and partially for Co^{III}, deviations from octahedral symmetry are reflected in the electronic spectra. The spectrum of the Fe^{III} complex consists of bands of both the low- and high-spin species. The optical electronegativity of the diethyldithiocarbamate ligand is found to be 2.5.

Introduction

In a preceding paper[1] we were able to show that the electronic spectra of diethyldithiocarbamate (dtc) complexes could be used for interpreting the structure of complexes of closed-shell central atoms. In the present paper we shall discuss, with the same purpose, the electronic spectra, d–d, and electron transfer transition, of dtc complexes of trivalent open-shell central atoms.

Evaluation of the spectral parameters. The d–d spectra were used to find Δ (d-orbital splitting parameter), B (Racah's interelectronic repulsion parameter), and Ds and Dt (the tetragonal splitting parameters). The d–d spectra were treated by the Tanabe and Sugano's procedure[2] assuming octahedral symmetry. The fitting of the spectra was successful for all complexes with the exception of $Mn(dtc)_3$ and $Fe(dtc)_3$. It was found that the d–d spectrum of $Mn(dtc)_3$ could be accounted for assuming tetragonal distortion ($O_h \rightarrow D_{4h}$). Following Ewald *et al.*[3,4] the spectrum of $Fe(dtc)_3$ was found to consists of bands of both the low- and high-spin species.

An attempt was made to account for the charge transfer bands. Many ways of doing this are now known.[5-7] We have chosen the method of Jørgensen.[8] The method consists of calculating:

$$(\pi \rightarrow t_{2g}) = W_1 - q(E-A) + \delta SPE$$
$$(\pi \rightarrow e_g) = W_1 + \Delta - q(E-A) + \delta SPE$$
$$(t_{2g} \rightarrow \pi^*) = W_2 + (q-1)(E-A) + \delta SPE$$
$$(e_g \rightarrow \pi^*) = W_2 - \Delta + (q-1)(E-A) + \delta SPE$$

where W_1 and W_2 are the energies of two molecular orbital levels determined relative to an assumed zero point of reference, (E–A) is the one-electron energy difference as function of the number of electrons in the d-subshell, and δSPE is the change in the spin-pairing energy occurring on excitation; for details see references.[8,9]

In the form put forward and used so far, this method gave satisfactory results;[8] however from a comparison with results of detailed M.O. calculations[10] it is evident that some modifications are necessary. A closer analysis reveals that for complexes which show $\pi \rightarrow \pi^*$ transitions of intra-ligand character, and if these transitions are almost unaffected by the presence of the central atom, the use of W_1 and W_2 as parameters constant for all complexes of that ligand is justified.

At present there is evidence (infrared, CH_2-p.m.r., electronic spectra),[1,11,12] that the π-electronic system of the dtc ligand is only slightly affected by the nature of the central atom. PPP electronic structure calculations of the ligand,[12] and on $Ni(dtc)_2$ [13] have shown that the important, for the low energy $\pi \rightarrow \pi^*$ transitions, π-levels comprise mainly atomic orbitals of the CS_2-group of dtc. The electron drift of the π-electrons of the sulphur atoms to or from the central atom is compensated by the electron drift of the nitrogen π-electrons.[12] The changes are subtle and have the effect of leaving the highest π-electron energy levels of the coordinated ligands almost unperturbed on coor-

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Table I. Electronic spectra of $M(dtc)_3$ and spectral parameters

	Transitions *			Δ	B	
	Exp.	Calcd.	Assignment	kK	kK	$\beta_{av.}$
$Cr(dtc)_3$	$15.5(2.58)^{a,b}$	15.5	$^4A_{2g}\rightarrow{}^4T_{2g}$			
d^3	$20.4(2.56)^{a,b}$	20.4	$^4A_{2g}\rightarrow{}^4T_{1g}(F)$	15.5	0.44	0.48
$CHCl_3$	—	38.8	$^4A_{2g}\rightarrow{}^4T_{1g}(P)$			
	$27\ (>3)^{a,b}$	27.9	$\pi\rightarrow t_{2g}$			
	$31.6(>3)^{a,b}$	30.6	$\pi\rightarrow e_g$			
		29.1	$t_{2g}\rightarrow\pi^*$			
$Mn(dtc)_3$	$6.0(<1)^c$	6.0	$^5B_{1g}\rightarrow{}^5A_{1g}$			
d^4	$16.0(\sim 2)^c$	16.0	$^5B_{1g}\rightarrow{}^5B_{2g}$	16.0	—	—
$CHCl_3$	$19.8(3.57)^d$	19.8	$^5B_{1g}\rightarrow{}^5E_g$		Ds = −1.40 kK	
		18.7	$a_{1g}\rightarrow\pi^*$		Dt = −0.08 kK	
	$28.2(3.98)^d$	28.7	$b_{2g}\rightarrow\pi^*$			
		27.4	$\pi\rightarrow e_g$			
	—	30.7	$\pi\rightarrow b_{1g}$			
	—	34.0	$\pi\rightarrow b_{2g}$			
	—	35.3	$e_g\rightarrow\pi^*$			
	—	44.0	$\pi\rightarrow a_{1g}$			
$Fe(dtc)_3$	$6.5(<1)^{c,f}$	5.6	$^5A_{1g}\rightarrow{}^4T_{1g}$		h.s.	
d^5	—	14.4	$^2T_{2g}\rightarrow{}^2A_{2g}$	12.8	0.51	0.47
$CHCl_3$	$17.1(3.1)^{a,c,f}$	16.7	$^2T_{2g}\rightarrow{}^2E_g$		l.s.	
		17.9	$\pi\rightarrow t_{2g}$ ls	17.0	0.45	0.41
	$19.7(3.3)^{a,e,f}$	19.2	$e_g\rightarrow\pi^*$ hs			
	$25.7(3.9)^{a,e,f}$	25.3	$\pi\rightarrow t_{2g}$ hs			
	$28.9(4.0)^{a,e,f}$	28.6	$\pi\rightarrow e_g$ 1s			
	$35.0(\ 4)^{e,f}$	35.2	$t_{2g}\rightarrow\pi^*$ hs			
		34.6	$t_{2g}\rightarrow\pi^*$ ls			
	$37.8(4.7)^{e,f}$	38.1	$\pi\rightarrow e_g$ hs			
$Co(dtc)_3$	$15.4(2.00)^a$	15.4	$^1A_{1g}\rightarrow{}^1T_{1g}$			
d^6	$20.9(2.78)^a$	20.9	$^1A_{1g}\rightarrow{}^1T_{2g}$	16.1	0.39	0.35
$CHCl_3$	$26.6^{**}(>4)^a$	26.7	$\pi\rightarrow e_g$			
	$31.0(4.30)^a$	31.0	$^1A_{1g}\rightarrow{}^1E_g$			
		31.3	$t_{2g}\rightarrow\pi^*$			
$Ru(dtc)_3$	16.9^d	16.9	$^2T_{2g}\rightarrow{}^2A_{2g}$, $^2T_{1g}$			
d^5	20.8 sh ^{d}	20.8	$^2T_{2g}\rightarrow{}^2E_g$	19.8	0.66	0.50
CCl_4		20.0	$t_{2g}\rightarrow\pi^*$			
	25.6 sh ^{d}	25.1	$\pi\rightarrow t_{2g}$			
	—	28.9	$^2T_{2g}\rightarrow{}^2A_{1g}$			
	—	34.5	$\pi\rightarrow e_g$			
$Rh(dtc)_3$	19.8^a	19.2	$^1A_{1g}\rightarrow{}^1T_{1g}$			
d^6	23.6^a	23.6	$^1A_{1g}\rightarrow{}^1T_{2g}$	20.1	0.57	—
		24.2	$t_{2g}\rightarrow\pi^*$			
$CHCl_3$	35.5^a	36.1	$\pi\rightarrow e_g$			
	39.7^a	—	$\pi\rightarrow\pi^*$			

[a] Ref. 16; [b] Ref. 17; [c] Ref. 3; [d] Ref. 18; [e] Ref. 19; [f] Ref. 4. $\pi\rightarrow t_{2g}$, for instance, designates electron transfer from the highest filled π—MO comprising mainly ligand π-orbitals, to t_{2g} of the central atom. Ground states of Cr, Mn, Fe, and Co complexes assigned according to Ref. 3. $W_1 = 29.3$ and $W_2 = 19.6$ kK. (E—A) = 2.7 kK for Cr, Mn, Fe, Co; (E—A) = 1.5 kK for Ru, Rh. Parameter D for calculating δSPE set equal to $91/(12B_{compl.})$.[9] hs, for the high spin species. ls, for the low spin species. * Position of band in kK (1000 cm^{-1}) and log ε in parenthesis. ** Mean value of two peaks located at 25.4(3.95) and 27.8(4.08) kK.[13]

dination. The alternative explanation of the finding that W_1 and W_2 are unaffected on coordination of the dtc ligand due to negligible π-bonding between the central atom and the ligands, is not convincing.

The use of constant values for (E—A), Δ, and D (for the evaluation of δSPE),[8,9] however, seems to blur out all differences in the charge transfer spectra. Hence, to cope with the problem, we have adopted the following procedure. Using the values for B(complex) and Δ obtained from the d—d spectra of each complex separately, we are in a position to calculate exactly δSPE.[9] Thus only W_1, W_2, and (E—A) remain to be determined. W_1 and W_2 should remain constant for all complexes if the invariancy of the π—π* separation of the appropriate ligand orbitals holds within ±2kK or less. (E—A) should be constant for a transition group,[8,9] but it should vary with the principal quantum number of the d-subshell.

Using the charge transfer bands of $Cr(dtc)_3$ and $Co(dtc)_3$, for which theory predicts and experiments[14,15] have shown to be nearly octahedral, we have calculated, on the basis of a tentative assignment of their spectra, $W_1 = 29.3$ and $W_2 = 19.6$ kK, and (E—A) = 2.7 kK. The same values of W_1 and W_2 were used, together with the bands of $Ru(dtc)_3$ and $Rh(dtc)_3$ to calculate (E—A) for the second transition group; (E—A) = 1.5 kK was obtained. Now with these pa-

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rameters the transition energies for the M(dtc)$_3$ may be reproduced. The results obtained are shown in the Table.

Discussion

As seen from the Table the method described in the preceding Section could well account for the electronic spectra of the dtc complexes of trivalent metal ions. Δ, and B, for Cr(dtc)$_3$ and Co(dtc)$_3$ are in excellent agreement with the parameters obtained by Martin *et al.*[3] A comparison of the data obtained with other experimental results disclosing the structure of the complexes may help in assessing the reliability of the assignment proposed and vice versa.

Cr(dtc)$_3$ dibutyl derivative was found to be nearly octahedral, with $g_{xx} = g_{yy} = g_{zz} = 1.980$.[14]

Mn(dtc)$_3$ must experience a considerable Jahn-Teller distortion.[3,20] As seen from the Table, a tetragonal distortion with Ds = –1.40 and Dt = –0.080 kK seems to account well for the observed spectrum. Since all quintet states have equal interelectronic repulsion energies (6A–21B),[21] B could not be evaluated. The first transition $^5B_1 \rightarrow {}^5A_1$ is symmetry and parity forbidden and this explains the observed low intensity ($\varepsilon < 10$).

Fe(dtc)$_3$ was found to consist, at room temperature, of a mixture from both a high- and a low-spin species. Taking the estimates of Martin *et al.*[3,4] for Δ and B, it is seen that the spectrum is composite of the spectra of the species present in solution. The pressure and temperature dependence of the spectrum, obtained by Martin *et al.*[4] supports the assignment proposed in the Table.

Co(dtc)$_3$ was assumed to be of octahedral symmetry. However there are some differences in the spectrum of the Co(dtc)$_3$ dialkyl derivatives at about 25-28 kK, which deserve some elaboration. For Co(S$_2$CNH$_2$)$_3$, Kida and Yoneda[17] have found a spectrum very nearly the same as the spectrum given in the Table. For Co(S$_2$CNEt$_2$)$_3$, however, Jørgensen[16] has found, in CHCl$_3$ solution, a splititng of the band at 26 kK into two components: 25.4(3.95) and 27.8-(4.08) kK. The same splitting was observed also in CCl$_4$ solution.[18] The crystal structure of Co(dtc)$_3$ turned out to be a quite distorted octahedron (C_{2v}).[15] This distortion was attributed to the constraint imposed on the geometry by the rigid nature of the dtc ligands and by the size of the bite angles at the metal atom (76°).[15] Keeping intact the assignment of the band at 26 kK as $\pi \rightarrow e_g$, the splitting of the e_g level in Co(dtc)$_3$ should be 2.4 kK. This is a rather small value and it suggests that, in solution, Co(dtc)$_3$ probably possesses higher symmetry than in the solid state. The merging of the two components into one for Co(S$_2$CNH$_2$)$_3$ supports this explanation.

Ru(dtc)$_3$ and Rh(dtc)$_3$ spectra fit rather well to the octahedral symmetry. Ru(dtc)$_3$, in the solid state. was found to deviate from octahedral arrangement of the surrounding six sulphur atoms.[22] The successful fit indicates that, as with Co(dtc)$_3$, the symmetry of the Ru(dtc)$_3$ may be higher in solution.

Using W$_1$ and W$_2$, the $\pi \rightarrow \pi^*$ transition (intraligand) is predicted at:

$$\nu(\pi \rightarrow \pi^*) = W_1 + W_2 - (E-A) = 48.9 - (E-A) \text{ kK}$$

hence, $(E-A) \approx 10$ kK, in order to reproduce the experimental value of 39 kK.[1] Charge separation effects are neglected in this treatment, hence $(E-A) \approx 10$ kK appears to be a reasonable value for a ligand comprising atoms with principal quantum number 2 and 3 for the valence shell electrons.

The optical electronegativity[23] of the ligand could be evaluated from the data collected in the Table. Values close to 2.5 were obtained. However the use of this value to reproduce the transition energies gives bad results due to the wide spreading of the optical electronegativity values for the central atoms. As seen from the collection of Jørgensen,[24] $\chi_{opt}(M)$ is given with an error of ±0.2, hence the position of the charge transfer band is located with ±6 kK.

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