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Complexes of Dithiocarboxylic Acids

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Dithiobenzoate ($C_6H_5CSS^- =$ dtb$^-$) and dithiophenylacetate ($C_6H_5CH_2CSS^- =$ dtpa$^-$) form, with transition elements, nonelectrolyte low-spin monomeric complexes $M^{II}L_2$ (square planar) or $M^{III}L_3$ (octahedral) (L = dtb, dtpa). Their electronic spectra show an intense absorption in the region 25–35 kK owing to the dithiocarboxylate system, which however does not prevent spectroscopic observation of the transition-metal-containing central chromophores of the complexes. Dithiocarboxylato ligands exert a large nephelauxetic effect; in the spectrochemical series of octahedral chromophores they are placed between H_2O and F^- and lie therefore close to but slightly higher than other dithio anions forming four-membered chelate rings.

Introduction

Dithiocarboxylates R–CSS$^-$ (R = alkyl, aryl) have been less widely investigated as ligands than other more well-known dithio anions[1–4] such as xanthates RO–CSS$^-$,[5] dithiocarbamates R_2N–CSS$^-$,[6–8] and dithiophosphates $(RO)_2PSS^-$,[9–13] etc., although some of their metal compounds, presumably possessing inner-complex structure, have been reported long ago.[14–18] This situation may be due to the low chemical stability of the free ligands and to their intense orange or red color which often masks spectral changes occurring on complexation, thus making investigation of the metal chromophores more difficult. An investigation of their properties is of potential interest, however, for two reasons: (i) the spectrochemical and nephelauxetic position of R–CSS$^-$ should be determined and compared with that of other dithio anions; (ii) among the few complexes hitherto known of C_6H_5CSSH, there is one of the so-called Ni(IV) compounds.[17,19] This fact suggests that dithiobenzoate and possibly other dithiocarboxylate ligands are capable, at least in some instances, of a peculiar reactivity, or possibly of noninnocent behavior, like the ligands (mnt, TDT, etc.) which form stable square-planar sulfur matrices,[20] although this behavior is usually associated with five-membered chelate rings[20–22] and not with four-membered ones, as are given by R–CSS$^-$ ligands.

We used two R–CSS$^-$ ligands (L$^-$), *i.e.*, dithiobenzoate, C_6H_5–CSS$^-$ (dtb$^-$), and dithiophenylacetate, $C_6H_5CH_2$–CSS$^-$ (dtpa$^-$). The metals include the nontransitional elements Na, Pb, and In, whose complexes were investigated in order to gain information about the spectral transitions of the ligands and the transitional elements Cr(III), Co(III), Ni(II), Pd(II), Pt(II), Rh(III), and Ir(III). Only the Na, Pb(II), and Ni(II) compounds were already described extensively in the literature,[14–18] while only vague reports were made of the cobalt and chromium compounds;[14,15] the dithiobenzoates of In(III), Cr(III), Co(III), Pd(II), Pt(II), Rh(III), and Ir(III) and the dithiophenylacetates of In(III), Cr(III), Co(III), Rh(III), Pd(II), Pt(II), and Ir(III) are reported here in detail for the first time.

Experimental Section

Preparation of Complexes.—The most convenient preparation of dithiocarboxylato complexes is (a) the reaction between NaL and a simple salt or a chloro complex of the given metal in water or alcohol–water. Occasionally, syntheses are performed successfully also by mixing alcoholic solutions of the metal compounds (b) with the acids LH in ether or (c) with PbL_2 in benzene. Methods b and c have disadvantages compared to method a, owing to the larger instability of HL used in method b and to the heterogeneity and low solubility of PbL_2 in benzene, as used in method c. Two typical examples of preparations from the Na salts in aqueous medium are reported below.

Tris(dithiophenylacetato)chromium(III).—A 24-g sample of CS_2 was added to a Grignard solution made up of 40 g of benzoyl chloride and 7.7 g of magnesium in 100 ml of anhydrous ethyl ether according to ref 15. After additional cooling, followed by 12 hr of standing at room temperature, the mixture was decomposed with ice and aqueous HCl; dithiophenylacetic acid was extracted with ethyl ether and shaken with an aqueous solution containing an approximately stoichiometric amount of Na_2CO_3. One thus obtains Na(dtpa) in the aqueous layer; the sodium salt is purified by repeated acidifications and extractions with ether followed by alkalinization and extraction with water. From the last aqueous extract, solid Na(dtpa) is recovered after careful evaporation *in vacuo*.[15]

To 150 ml of a 0.1 *M* aqueous solution of Na(dtpa), 50 ml of 0.1 *M* $CrCl_3 \cdot 6H_2O$ was added at room temperature. A brownish

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TABLE I

ANALYTICAL DATA[a] OF DITHIOCARBOXYLATO COMPLEXES: $dtb^- = C_6H_5CSS^-$; $dtpa^- = C_6H_5CH_2CSS^-$

Substance[d]	Color	Mp, °C	Analyses, %								Previous lit. reports, ref
			C		H		S		Metal		
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$Cr(dtb)_3$	Red-brown	258–259	49.29	49.31	2.95	3.15	37.59	37.39	10.16	9.75	14
$Cr(dtpa)_3$	Green-brown	150	52.04	51.96	3.82	4.02	34.73	34.91	9.39	9.21	
$Co(dtb)_3$	Red-brown	236	48.62	48.92	2.91	3.02	37.09	37.47	11.36	10.63	14
$Co(dtpa)_3$	Dark green	155–156	51.40	50.69	3.72	3.55	34.30	32.98	10.58	10.78	15
"$Ni_2S_2(dtb)_4$"	Violet	198	42.32	42.67	2.53	2.75	40.35	37.69	14.77	16.89	17
$In(dtb)_3$	Red-orange	149–150	43.89	44.05	2.63	2.62	33.48	33.35	19.98	19.98	
$In(dtpa)_3$	Golden yellow	145–146	46.75	46.68	3.43	3.53	31.20	30.95	18.62	18.84	
$Rh(dtb)_3$[b]	Red-brown	315	44.82	44.27	2.68	3.06	34.19	34.16	18.29	18.51	
$NH_4[Rh(dtb)_2Cl_2]$[c]	Purple-red	235	33.74	33.88	2.83	2.78	25.73	25.65	20.65	19.59	
$Rh(dtpa)_3$	Orange	163	47.66	47.62	3.50	3.39	31.81	31.52	17.01	16.47	
$Pd(dtb)_2$	Red-violet	269	40.69	40.67	2.44	2.49	31.04	30.62	25.82	25.05	
$Pd(dtpa)_2$	Brown-yellow	185–186	43.55	44.20	3.19	3.42	29.06	28.61	24.18	23.77	
$Ir(dtb)_3$	Brown-red	80	38.68	38.75	2.31	2.15	29.51	29.90	29.48	28.86	
$Ir(dtpa)_3$	Red-brown	158–160	41.53	41.83	3.05	2.98	27.72	28.29	27.69	26.90	
$Pt(dtb)_2$	Dark green	305	33.52	34.22	2.00	2.18	25.57	24.25	38.89	39.35	
$Pt(dtpa)_2$	Green-blue	255–256	36.28	36.44	2.66	2.89	24.21	24.50	36.83	36.17	

[a] Organic microanalysis by Laboratorium A. Bernhardt, Mülheim, Germany. [b] From alcoholic $RhCl_3$ hydrate + aqueous Na(dtb). [c] From $(NH_4)_3RhCl_6$ and Na(dtb) in water. Calcd: N, 2.81; Cl, 14.23. Found: N, 2.68; Cl, 14.10. [d] Other complexes investigated spectroscopically in the present work include blue $Nidtb_2$, mp 220–223°;[17] dark red $Ni(dtpa)_2$, mp 135°;[4] red $Pb(dtb)_2$, mp 204–205°;[14] yellow $Pb(dtpa)_2$, mp 149°.[15] The nickel (II) complexes give readily 1:2 pyridine adducts which are paramagnetic ($\mu \sim 3.2$ BM): $Ni(dtb)_2 \cdot 2py$, brown crystals giving highly dichroitic red-green solutions in organic solvents; $Ni(dtpa)_2 \cdot 2py$, yellow-brown crystals.[4]

green precipitate formed immediately, which can be recrystallized from cyclohexane to give olive green lamellar crystals of $Cr(dtpa)_3$ (mp 150°) in almost quantitative yield. The complex is moderately soluble in chloroform, benzene, and paraffins. For analysis, see Table I.

Bis(dithiobenzoato)palladium(II).—An ethereal solution of C_6H_5–CSSH obtained after hydrolysis of the reaction product of C_6H_5MgBr and CS_2, according to ref 15, is shaken with dilute aqueous Na_2CO_3. Sodium dithiobenzoate passes into the aqueous layer and is recovered after evaporation as an orange solid. Crude C_6H_5–CSSNa (1.76 g, 0.01 mol) is dissolved in 100 ml of water and added dropwise to 100 ml of 0.01 M K_2PdCl_4 at room temperature with moderate stirring. A dark brown precipitate formed, which is crystallized several times from toluene. The resulting brown-violet plates have a melting point of 269° and solubility is rather low in most organic solvents ($\sim$0.1 mM in $CHCl_3$). For analysis, see Table I.

Table I lists the substances prepared by us, including analyses, melting points, and previous literature reports.

Solubility.—The complexes have varying solubilities in nearly all organic solvents, both polar and nonpolar, but except the salt-like Na compounds, are insoluble in polar protic solvents. The least soluble are the Pd(II) and Pt(II) compounds: bis(dithiophenylacetato)platinum(II) is so sparingly soluble that we were not able to measure its absorption spectrum with sufficient accuracy. The indium(III) and cobalt(III) compounds are the most soluble ones.

Molecular Weights.—Measurements were performed in benzene solutions with a Mechrolab Model 301 A vapor pressure osmometer. Accuracy was often poor because of low soubility, which in some instances was so low as to prevent measurements. Typical results for molecular weight were: $Cr(C_6H_5CSS)_3$: found in a 1.205% solution in benzene, 488 $\mp$ 5; calcd, 511; $Cr(C_6H_5CH_2CSS)_3$: found in a 0.126% solution in benzene, 545 $\mp$ 40; calcd, 547; $Pd(C_6H_5CSS)_2$: found in a 0.67% solution in benzene, 390 $\mp$ 70; calcd, 407.

Spectral Measurements.—Ultraviolet and visible spectra were recorded with a Beckman DK-1A apparatus on solutions in organic solvents (mostly chloroform or benzene, also occasionally ether, ethanol, CCl_4, cyclohexane; water was used for the free acids and the Na salts). The investigated ranges of concentrations were 10^{-2}–10^{-3} M for the visible and 10^{-3}–10^{-5} M for the ultraviolet region, using calibrated 1-cm or 1-mm quartz cuvettes. All substances followed Beer's law within experimental accuracy, except the pyridine adducts of the Ni(II) complexes, which tended to dissociate in dilute solutions. No large spectral difference was observed in various solvents, as is shown, *e.g.*, by Table II which contains a record of spectral data of the acids in largely different media; even less significant differences occurred in the spectra of the complexes. For the transition metal complexes, also the visible reflectance spectra were measured (Beckman DK spectroreflectometer accessory) and found again substantially coincident with the corresponding absorption spectra.

Magnetic Measurements.—These were performed on solid polycrystalline samples with a Gouy balance over a temperature interval from liquid N_2 to room temperature. All substances listed in Table I proved to be diamagnetic, except the Cr(III) compounds which reveal the paramagnetism associated with three unpaired electron spins ($Cr(dtb)_3$, $\mu_{eff} = 3.90$ BM; $Cr(dtpa)_3$, $\mu_{eff} = 3.88$ BM) and Weiss constant close to 0°. Also the pyridine adducts $Ni(dtb)_2 \cdot 2py$ and $Ni(dtp)_2 \cdot 2py$ are paramagnetic, roughly corresponding to two unpaired electron spins.

Results

Preparation and Properties of Dithiocarboxylato Complexes.—The ligands $C_6H_5CSS^-$ and $C_6H_5CH_3CSS^-$ readily form inner-complex, nonelectrolyte compounds with the transitional and nontransitional elements listed in Table I, corresponding to the general formulas $M^{II}L_2$ and $M^{III}L_3$ for the bi- and trivalent elements, respectively: the only exception is rhodium(III), which can form with dtb^-, according to the experimental conditions of preparation, either neutral $Rh(dtb)_3$ or the anionic $Rh(dtb)_2Cl_2^-$ complex. In any case however, the central metals are to be considered as tetracoordinated when bivalent in $M^{II}L_2$ or hexacoordinated when trivalent in $M^{III}L_3$ or in $Rh^{III}L_2Cl_2^-$. Moreover, the magnetic behavior is always of the low-spin type, suggesting that the geometry of coordination is square planar for the transition metals M^{II} (=Ni, Pd, Pt), which have $(nd)^8$ configuration, or pseudo-octahedral for M^{III} (=Cr, Co, Rh, Ir), having $(nd)^3$ or $(nd)^6$ configuration. The low solubility of some complexes might be taken as suggestive of polymeric structure, as has been reported for other complexes of sulfur-containing ligands,[4,23] but this possibility is ruled out by

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(23) A. Ripamonti, private communication.

molecular weight determinations showing monomeric nature, as well as by the fact that Beer's law is strictly obeyed in solution and by X-ray structure determinations (see next section). Therefore formulas $M^{II}L_2$ and $M^{III}L_3$ represent correctly not only the stoichiometric composition, but also the true molecular complexity of dithiocarboxylato complexes.

The ligand moiety appears to be considerably stable in the complexes (which, *e.g.*, all melt without decomposition) contrary to the low chemical stability of the free ligands; such an increased stability occurring upon chelation is not infrequent among organic ligands. The central metals are stable in their most common oxidation state, whenever appropriate for formation of neutral nonelectrolyte complexes; Co(II) salts are very easily autoxidized in the presence of dithiocarboxylates and invariably give the Co(III) complexes (compare ref 14 and 15). Peculiar aspects occur in the behavior of Ni(II) and Rh(III) with dtb^-: deep blue $Ni(dtb)_2$, although stable as the pure solid also in air, does not stand mild oxidative treatments in solution and yields a well-defined violet product ("$Ni^{IV}{}_2S_2(dtb)_4$") which, although long known[17] and well characterized, is still subject to controversy as to its structure; it has been formulated as an Ni(IV) derivative[17] or as an Ni(II) chelate of a disulfide derivative of dithiobenzoic acid.[19] Rhodium(III) gives two kinds of dtb complexes according to the starting product (either simple rhodium(III) chloride or a chlororhodate(III) complex), while other metals give the same complex $M^{II}L_2$ or $M^{III}L_3$ irrespective of the nature of the M salt or complex reacting with L. Besides, the yield in the preparation of both Rh(III) compounds is very low, contrary to the definite course and high yield in the preparation of other dithiocarboxylato complexes, and considerable amounts of ill-defined by-products are obtained, which also probably contain some Rh(I) species, since they evolve $[Rh^I(CO)_2Cl]_2$ on treatment with CO.

Electronic Spectra. For classification purpose we divide the absorption bands into three different groups, as follows.

(a) In the ultraviolet region, the free ligands (acids and Na salts) have one or more intense n → V bands between 29 and 34 kK, followed by the benzenoid bands (secondary band at 37–40 kK; primary band at 45–48 kK). The same spectral patterns are repeated, with minor changes, in the spectra of all investigated complexes.

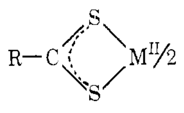
(b) In the region between approximately 22 and 30 kK, bands sometimes appear which are absent from the spectra of the free ligands, and we tentatively classify them as charge transfers.

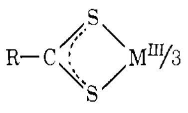
(c) In the visible region ($\lesssim$22 kK) weaker absorptions occur, which follow rather closely the spectral patterns (d–d bands) expected for metal chromophores with square-planar and pseudo-octahedral coordination.

A survey of experimental data, following the above tentative classification, is presented in Tables II and III and Figures 1–4.

Discussion

Properties and Structure of Dithiocarboxylato Complexes.—The established monomeric nature of the dithiocarboxylato complexes, together with the occurrence of only one kind of donor atoms, *i.e.*, sulfur, in the relatively simple structure of the ligands, available to accomplish the fourfold coordination in $M^{II}L_2$ and the sixfold coordination in $M^{III}L_3$, imply necessarily that dithiocarboxylates form four-membered chelate rings such as





M^{II} = Ni, Pd, Pt M^{III} = Cr, Co, In, Rh, Ir

Dithiocarboxylates are therefore able to act as bidentate chelating ligands like other dithio anions, such as dithiocarbamates,[6–8] xanthates,[5] and dithiophosphates,[7,13] etc. This is confirmed by the preliminary X-ray data of Bonamico and co-workers on the structure of $Pd(dtb)_2$[24] and of $Cr(dtb)_3$[25] showing actually square-planar and respectively trihedral quasi-octahedral coordination; it is noteworthy that in dtb the whole ligand molecule is coplanar with a relatively short C–C distance between C_6H_5 and CS_2^- of 1.46–1.47 Å, which is indicative of conjugation between the two entities[24] (see Figure 1).

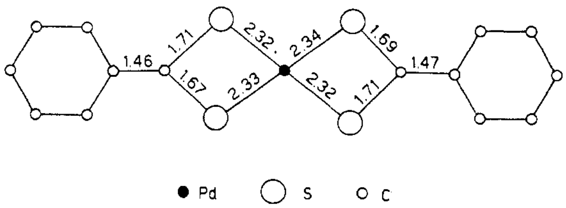


Figure 1.—Schematic structure of one of the two independent molecules in the elementary cell of $Pd(dtb)_2$ (from Bonamico[16]).

On the whole, the chemistry of dithiocarboxylato complexes is very similar to the chemistry of transition metal complexes with the other above-mentioned dithio anions, even in smaller details such as the formation of pseudo-octahedral 1:2 adducts of the Ni(II) complexes with pyridine. Peculiarities can be seen, *e.g.*, in the easy oxidation of $Ni(dtb)_2$; it is not yet clear whether this behavior is to be interpreted as a consequence of peculiar reactivity of the ligand, *i.e.*, of its possible transformation into a disulfide-type derivative[19] or of possible oxidation of the whole system of π-conjugated sulfur ligands as in the mnt systems;[20] we just notice from the experimental circumstances that such peculiar behavior is paralleled in $Ni(dtb)_2$ by characteristic features of the charge-transfer spectrum (see next paragraph) and is limited essentially to the Ni–dtb system. The slight tendency of Rh(III) to enter the common reaction scheme leading to $M^{III}L_3$ species for tervalent metals can be traced back to the known ten-

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(24) M. Bonamico and G. Dessy, *Chem. Commun.*, in press.

(25) M. Bonamico and G. Dessy, unpublished work.

TABLE II

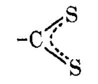
ABSORPTION SPECTRA OF FREE DITHIOCARBOXYLATO LIGANDS[a]

Substance	Solvent	n → π	n → V	K	Benzene bands
H(dtpa)[b]	Ether	21.3 (1.34)	33.4 (3.73)		39.6 (3.40)
H(dtpa)[c]	Cyclohexane	21.4 (1.42)	33.6 (3.81)		[36.4] (3.35)
H(dtpa)[d]	CCl_4	21.2 (1.49)	33.6 (3.84)		[35.1] (3.44)
Na(dtpa)[e]	Water	[21.7] (1.71)	29.7 (3.99)		[42.2] (3.53); 48.4 (4.11)
H(dtb)	Ether	19.2 (1.81)	[30.8] (3.67)	33.9 (3.98)	[40] (3.34); 45.5 (3.78)
H(dtb)	Cyclohexane	18.9 (1.80)	[30.8] (3.54)	34.2 (3.91)	[40] (3.15); 44.5 (3.53)
H(dtb)	CCl_4	19.1 (1.63)	[30.8] (3.66)	33.8 (3.98)	
Na(dtb)	Water	20.8 (2.15)	28.6 (3.75)	34.5 (3.72)	[40.8] (3.52); 46.4 (3.94)

[a] $dtpa^- = C_6H_5CH_2CSS^-$; $dtb^- = C_6H_5CSS^-$; band maxima $\bar{\nu}$ in kK (log E_{mol}); shoulders in brackets. [b] Shoulder at 20 (1.76) and 24.7 (1.10). [c] Shoulder at 19.8 (1.22) and 24.1 (1.42). [d] Shoulder at 20.0 (1.30) and 23.8 (1.33). [e] Shoulder at 25.3 (2.01).

dency of rhodium to give Rh(I) derivatives in square-planar coordination.

Absorption Spectra. Ligand Systems.—The free $dtpa^-$ ligand containing two separate chromophoric systems, the $-CSS^-$ and the phenyl group, has four distinct bands: (i) a low-intensity n → π band of the thiocarbonyl group at ~21.7 kK (log E_{mol} ~ 1.7), which is responsible for the red color of this class of compounds and is similar in position and intensity to the n → π band of several other thiocarbonyl compounds (*e.g.*, 16.7 in thiobenzophenone,[26] 19.6 kK in thioacetylcyclohexane,[27] etc.); (ii) an intensive (log E_{mol} ~ 4) band at 29.7 kK, which we assign as the first n → V transition within the conjugate



group; and (iii) and (iv) the two benzene bands (primary band 48.4 kK; secondary band 42.2 kK). The assignment of the band at 29.7 kK is further supported by the results of a semiempirical PPP calculation of the $-CSS^-$ chromophore, whose details will be reported elsewhere.[28]

The free dtb^- ion has a similar spectrum (see Figure 4 and Table II), except that it has an additional ultraviolet band at ~34 kK, which is not benzenoid, and yet this band is missing from $dtpa^-$, where the two chromophores, *i.e.*, the phenylic and the dithiocarboxylic groups, are isolated by a $-CH_2-$ group; we are therefore inclined to assign the band at ~34 kK to the effect of conjugation between the C_6H_5 and the CS_2^- groups or to an "intramolecular charge transfer" according to the model by Nagakura.[29,30] Quite similar absorption patterns occur also in the metal complexes of dtb. With nontransitional elements like lead and indium, the benzenoid bands are practically unchanged, and the n → π band is of somewhat larger intensity, while a more significant change occurs in the n → V bands of both ligands and in the conjugation band of dtb, which appear split up, and give rise, in the region between *ca.* 26 and 34 kK, to two bands in complex dithiophenylacetates and usually three in complex dithiobenzoates (see Figures 2 and 5); so the band at 29.7 kK (3.99) of Na(dtpa) is split into two bands at 28.2 kK (3.84) and 31.8 kK (4.08) in $Pb(dtpa)_2$, and the two bands at 28.6 and 34.5 kK in Na(dtb) correspond to a triplet (26.4, 30.9, and 34.1 kK) in $In(dtb)_3$. In complexes of transitional elements, the same spectral patterns are repeated rather regularly in the 26–34-kK region; when occasionally an additional band appears, we confidently assume that a charge-transfer transition to the central metal occurs in the same region. Benzenoid bands are usually less evident in transition metal complexes because they are often masked by short-wavelength charge transfers, and also the n → π bands around 21–25 kK are no longer clearly discernible in the presence of either charge-transfer or ligand-field bands.

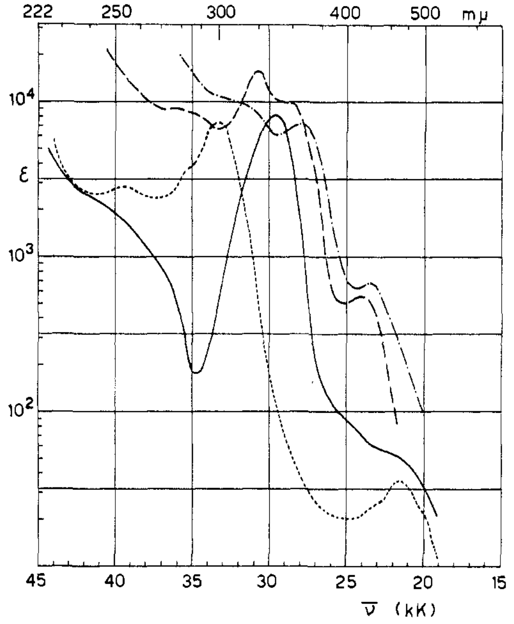


Figure 2.—Absorption spectra of compounds of dithiophenylacetic acid (H(dtpa)) with nontransitional elements: · · · ·, H(dtpa) in CCl_4; ——, Na(dtpa) in H_2O; —·—·—·, $Pb(dtpa)_2$ in C_6H_6; – – – –, $In(dtpa)_3$ in $CHCl_3$.

Octahedral Complexes.—The $M^{III}S_6$ chromophores of transition metals behave practically as octahedral and have the spectrum predicted by ligand-field theory for the appropriate low-spin d^n configurations in octahedral environment, or at least the lower frequency part ($\lesssim$25 kK) of such a spectrum; thus we have $^4A_{2g} \rightarrow {}^4T_{2g}$ at 16.85 kK and $^4A_{2g} \rightarrow a^4T_{1g}$ at 20.6 kK in $Cr(dtpa)_3$ (but the latter transition is not observed, and the former is just an uncertain shoulder at ~16 kK in $Cr(dtb)_3$), and $^1A_{1g} \rightarrow {}^1T_{1g}$ at 16.95 kK in $Co(dtpa)_3$; similarly, only the first spin-allowed d–d

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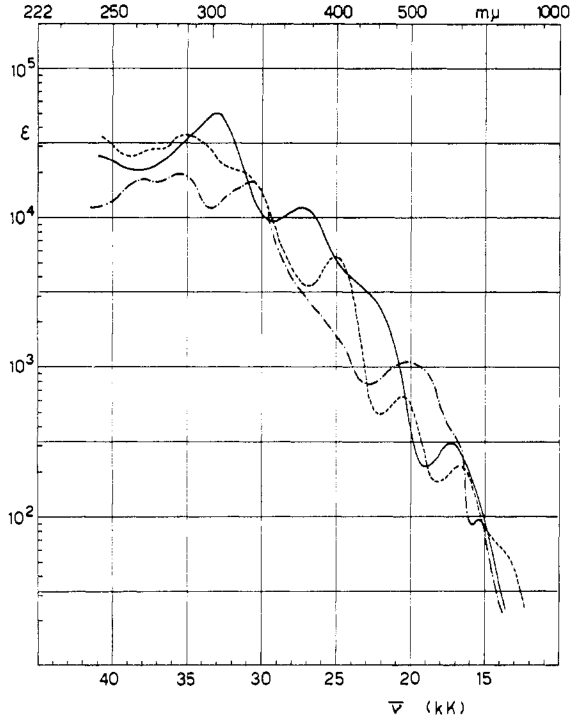

Figure 3.—Absorption spectra of transition metal complexes of dithiophenylacetic acid (H(dtpa)) in chloroform: · · · · ·, $Cr(dtpa)_3$; ——, $Co(dtpa)_3$; —·—·—·, $Ni(dtpa)_2$.

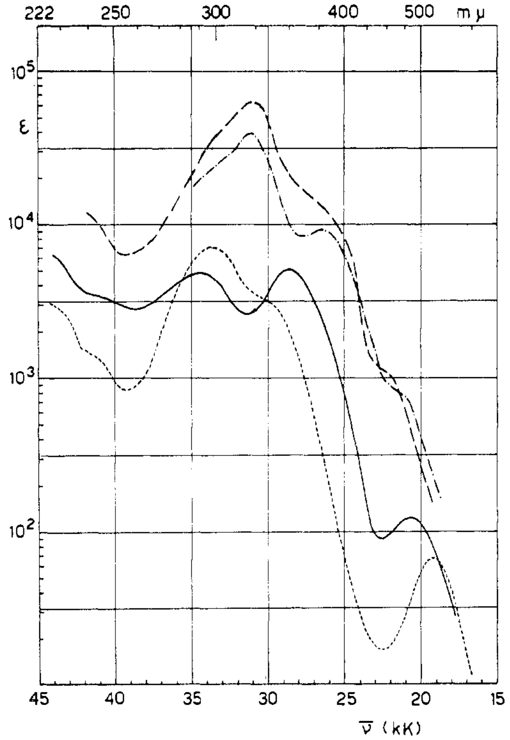

Figure 4.—Absorption spectra of compounds of dithiobenzoic acid (H(dtb)) with nontransitional elements: · · · · ·, H(dtb) in ether; ——, Na(dtb) in H_2O; —·—·—·, $Pb(dtb)_2$ in C_6H_6; – – – –, $In(dtb)_3$ in $CHCl_3$.

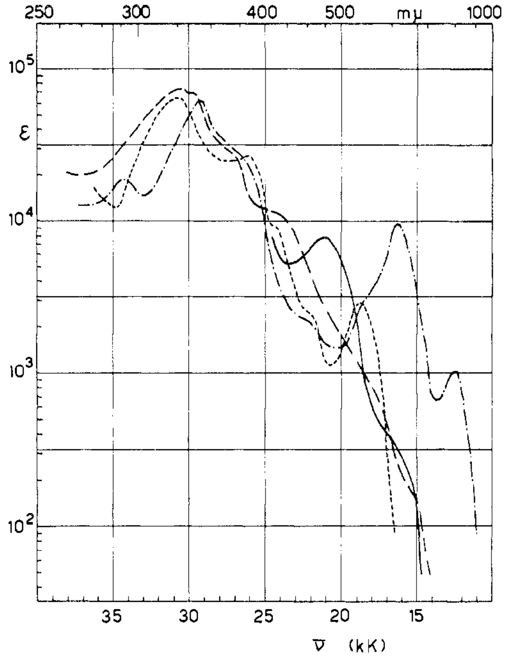

Figure 5.—Absorption spectra of transition metal complexes of dithiobenzoic acid (H(dtb)) in chloroform: —·—·—·, $Ni(dtb)_2$; · · · · ·, $Pd(dtb)_2$ (in C_6H_6); — —, $Cr(dtb)_3$; ——, $Co(dtb)_3$.

band is observed in the low-spin d^6 complexes $Co(dtb)_3$, $Rh(dtb)_3$, $Rh(dtb)_2Cl_2^-$, $Rh(dtpa)_3$, $Ir(dtb)_3$, and $Ir(dtpa)_3$. The bands are not particularly intensive, log E_{mol} being usually in the range 2–3. Spin-forbidden d–d transitions are not evident. The observed Δ values place the dithiocarboxylato ligands near the upper end of the spectrochemical series of chelating sulfur anions: *e.g.*, $\bar{\nu}_1$ (=Δ) is 14.3 kK for $Cr(dtp)_3$,[1] 15.5 kK for $Cr(dtc)_3$,[1] and 16.1 kK for $Cr(exan)_3$,[5,31] compared with 16.0–16.8 for Cr(III) dithiocarboxylates. Thus the spectrochemical series of sulfur ligands in octahedral chromophores (eq 5 in ref 1) can be completed as $(RO)_2PSS^- < R_2NCSS^- < ROCSS^- < RCSS^-$. For comparison with other donor atoms, $Cl^- < F^- <$ urea $< RCSS^- < H_2O \sim ox^{2-} < NR_3$.

There is a small spectrochemical difference between octahedral complexes of dtb and dtpa, Δ being slightly but distinctly higher in dtpa than in dtb complexes. Such spectrochemical ordering is well in agreement with Jørgensen's view[1] that the spectrochemical position of sulfur ligands should be higher, the lower the availability of ligand electrons for dative π bonds, or the lower the C–S (or P–S) bond order. In the present case, the C–S bond order should approach 1.5 but might possibly be lower in dtb because of conjugation between $-CSS^-$ and the phenyl group.

The nephelauxetic effect can be observed in $Cr(dtpa)_3$, where $\beta_{35} = 0.35$, quite in line with other sulfur-containing chelating agents, which give a very pronounced nephelauxetic decrease of β.[1,32] From the spectra of the d^6 complexes, the x_{opt} values were determined, after the usual corrections, according to $30(x_{opt}(S) - x_{opt}(M)) = \bar{\nu}_{ct} - \Delta + D$ kK, as 2.60 ∓ 0.08 for S of dtb^- and 2.65 ∓ 0.05 for S of $dtpa^-$. Also these values are quite close to those of other thio ligands,[32,33] the slightly lower value of dtb^- being probably due to more extensive

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TABLE III

ABSORPTION SPECTRA OF METAL DITHIOCARBOXYLATES[a]

Substance	Solvent	d–d	Charge transfer	n → V	K	Benzene bands
$Pb(dtpa)_2$[b]	C_6H_6			28.2 (3.84); 31.8 (4.08)		[35.2] (4.31)
$In(dtpa)_3$[c]	$CHCl_3$			28.2 (4.00); 30.4 (4.26)		[35.8] (3.95)
$Cr(dtpa)_3$	$CHCl_3$	16.8$_5$ (2.34);[d] 20.6 (2.80)[e]	24.9 (3.69);	[31.4] (4.27); 34.5 (4.53)		[36.5] (4.43)
$Co(dtpa)_3$	$CHCl_3$	16.9$_5$ (2.44)[f]	22.4 (3.45)	27.4 (4.11); 33.1 (4.72)		[39.4] (4.32)
$Rh(dtpa)_3$	$CHCl_3$	[23.8] (3.48);[f] 26.2 (3.73)[g]	[31.2] (4.16)	[34.4] (4.47); 38.4 (4.80)		[39.2] (4.59)
$Ir(dtpa)_3$	$CHCl_3$	[19.8] (2.99); [22.0] (3.35)		26.7 (3.79); [32.8] (3.96)		39.5 (4.54)
$Ni(dtpa)_2$[h]	$CHCl_3$	14.9 (1.98);[i] 17.2 (2.61);	19.8 (3.11);	30.3 (4.23); 35.5 (4.15)		[38.4] (4.16)
$Pd(dtpa)_2$	C_6H_6	[22] (3.04)[i] 25.0 (3.60);	30.5 (3.94);	33.5 (4.40); 34.7 (4.42)		
$Ni(dtpa)_2(py)_2$[j]	$CHCl_3$	10.7 (1.5);[p] 16.7 (1.79)[q]				
$Pb(dtb)_2$[k]	C_6H_6			26.4 (3.99); 30.9 (4.70)	34.1 (4.46)	
$In(dtb)_3$[l]	$CHCl_3$			26.0 (4.09); 30.9 (4.83)	[33.0] (4.59)	[40.8] (4.02)
$Cr(dtb)_3$[m]	$CHCl_3$	16.0 (2);[d] 18.5 (3)[e]	[24.5] (3.99);	[26.4] (4.15); [29.1] (4.73);	31.1 (4.79)	40.0 (4.73)
$Co(dtb)_3$	$CHCl_3$	16.0 (2.3)[f]	21.1 (3.91)	[26.4] (4.25); 28.8 (4.58)	31.8 (4.77)	(39.2) (4.20)
$Rh(dtb)_3$	$CHCl_3$	[19.6] (2.96); [21.2] (3.28)		25.6 (3.82); 29.9 (4.21)	32.7 (4.24)	
$NH_4[Rh(dtb)_2Cl_2]$	$CHCl_3$	18.7 (3.12); 19.6 (3.15)	23.5 (3.58)	27.8 (3.96); 30.5 (4.64)		
$Ir(dtb)_3$	$CHCl_3$	[18.8] (2.86); [23.5] (3.38)		29.4 (4.22); 33.4 (4.41)	[34.7] (4.39)	
$Ni(dtb)_2$[n]	$CHCl_3$	13.2 (2.99);[i] [15.2] (3.32);	16.9 (4.03)	[27.0] (4.45); 29.2 (4.90)	34.2 (4.19)	
$Pd(dtb)_2$	C_6H_6	18.2 (3.49);[i] [22.2] (3.41)	24.0 (4.01);	26.0 (4.36); 31.0 (4.77)	33.5 (4.40)	
$Pt(dtb)_2$[o]	$CHCl_3$	15.3 (3.04); 18.7 (3.29)	23.2 (3.80);	26.3 (4.20); 31.7 (4.40)	[35.7] (4.29)	
$Ni(dtb)_2(py)_2$	$CHCl_3$	10.5 (~2);[p] 14.7 (~2.3)[q]				
"$Ni_2S_2(dtb)_4$"	$CHCl_3$	17.7 (4.16); 19.0 (4.26);	23.0 (3.93)	[26.0] (4.20); 29.8 (5.09)	33.9 (4.61)	[40.0] (4.38)

[a] $dtpa^- = C_6H_5CH_2CSS^-$; $dtb^- = C_6H_5CSS^-$; band maxima $\bar{\nu}$ in kK (log E_{mol}); shoulders in brackets. [b] n → π at 24.0$_5$ (2.91). [c] n → π at 24.4 (2.75). [d] $^4A_{2g} \rightarrow {}^4T_{2g}$. [e] $^4A_{2g} \rightarrow a^4T_{1g}$. [f] $^1A_{1g} \rightarrow {}^1T_{1g}$. [g] $^1A_{1g} \rightarrow {}^1T_{2g}$. [h] Shoulder at 24.4 (3.15). [i] $^1A_{1g} \rightarrow {}^1A_{2g}$ (D_{4h}). [j] Shoulder at 22.0 (2.5). [k] n → π at 21.3 (2.91). [l] n → π at 22.4 (3.20). [m] For ligand field assignment, see above. [n] Shoulder at 18.2 (3.67) and 23 (3.31). [o] Shoulder at 20.8 (3.44) and 33.9 (4.37). [p] $^3A_{2g} \rightarrow {}^3T_{2g}$. [q] $^3A_{2g} \rightarrow a^3T_{1g}$.

conjugation within the π system of the ligand. Thus the whole of the spectrochemical properties of the octahedral complexes of dithiocarboxylates fits well into the conventional ligand-field scheme and into the usual classification of the donor properties of the ligand atoms.[1]

Square-Planar Complexes.—The spectrochemical behavior of the four-coordinated complexes $M^{II}L_2$ of the d^8 configuration is somewhat different and does not fit as well into the current interpretative schemes. The most evident example of less usual behavior occurs in $Ni(dtb)_2$ having the first d–d band $\bar{\nu}_1$ as low as 13.2 kK and very intensive ($E_{mol} = 1.0 \times 10^{-3}$) and furthermore a broad band peaked at 16.2 kK ($E_{mol} = 9.5 \times 10^3$) with several shoulders, which we tentatively assign, particularly in consideration of its very high intensivity, to a charge transfer. Such a low value of $\bar{\nu}_1$ places dtb^- lower than any other sulfur ligand except mnt^{2-} ($\bar{\nu}_1$ of $Ni(mnt)_2^{2-}$ is 11.0 kK[12]) in the spectrochemical series of quadratic Ni(II) chromophores, the next smallest observed value of $\bar{\nu}_1$ being that of bis(diphenyldithiophosphinato)nickel at 14.3 kK.[34,35] This trend, placing dtb^- in a spectrochemical position comparatively lower than other sulfur ligands with respect to the corresponding octahedral spectrochemical series, is not limited to the Ni(II) complexes discussed above but is also observed, although less pronounced, in other square-planar complexes containing dtb: red-brown $Pd(dtb)_2$ has $\bar{\nu}_1$ at 18.2 kK, much lower than $Pd(dtp)_2$ ($\bar{\nu}_1 = 21.8$ kK), which is the lowest end of Jørgensen's spectrochemical scale in ref 1; again, the first band of $Pd(dtb)_2$ has a very large intensity ($E_{mol} \sim 3 \times 10^3$), a fact suggesting that it might be charge transfer in character rather than ligand field (the first d–d band could then be masked within the envelope of the band at 18.2 kK). $Pt(dtb)_2$ has the first d–d band at 15.3 kK ($E_{mol} = 1.3 \times 10^3$), again much lower than $\bar{\nu}_1$ of $Pt(dtp)_2$ (23.8 kK).[1] The dtpa complexes behave, on the contrary, much closer to what would be expected from the spectrochemical behavior known of the octahedral chromophores, although not quite exactly in the same way; thus, red-brown $Ni(dtpa)_2$ has $\bar{\nu}_1$ at 14.9 kK (higher than, *i.e.*, $Ni(dtp)_2$ at 14.5 kK[1] but lower than $Ni(dtc)_2$ at 15.8 kK,[1] whereas $dtpa^-$ in the octahedral spectrochemical series is higher than dtc^-) and with a normal intensity ($E_{mol} = 90$). $Pd(dtpa)_2$ has only a shoulder around 22 kK, which compares favorably with 21.8 of $Pd(dtp)_2$ and 22.2 of $Pd(dtc)_2$;[1] $Pt(dtpa)_2$, as noted previously, is so insoluble that no reliable record of its spectrum could be obtained. The x_{opt} value still appears rather low in quadratic dtpa complexes; although charge-transfer bands cannot be identified with certainty, they are probably strongly intermixed with the π–π^* transitions of the $-CSS^-$ group and possibly with the higher d–d transitions participating in the 24.4-kK band, in the shoulder at 17.2 and 19.8 of $Ni(dtpa)_2$, and in the large peak at 25.0 of $Pd(dtpa)_2$.

The spectrochemical behavior of dithiocarboxylate ligands seems therefore to lend itself much less to a simple classification in the case of square-planar complexes than of the octahedral ones. As found also in other cases, the spectrochemical series cannot well be transferred from octahedral to square-planar complexes;[1] in the present case, deviations appear to be particularly large with dtb and still noticeable, even if

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not so large, with dtpa. Such unusual spectrochemical behavior clearly parallels the unusual features of chemical reactivity, *i.e.*, easy oxidizability, of Nidtb$_2$. At present, our experimental data do not indicate any simple, obvious interpretation of this behavior; it is probably to be related to the extension of π conjugation in dtb over a larger framework, including both the $-CSS^-$ group and the phenyl ring (actually, Bonamico's work shows that the C–C distance between C_6H_5 and CS_2^- is short enough to suggest conjugation between the two groups), and possibly also to intraligand conjugation effects occurring between both L units in a square-planar complex, *i.e.*, to the same cause leading to the well-known peculiar chemical and spectrochemical properties of complexes containing stable square-planar matrices.[20]

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An Investigation of Crystalline Paramagnetic Salts of Nitrosyldisulfonate Ion

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The preparation and determination of several salts of the free radical nitrosyldisulfonate ion are reported. These all have one unpaired electron per anion, as indicated by magnetic susceptibility measurements. The pure salts gave broad epr signals, but after dilution with a diamagnetic solid, or after partial decomposition, hyperfine splittings appeared.

The violet free radical nitrosyldisulfonate ion, $ON(SO_3)_2^{2-}$, has been the subject of numerous kinetic and electron paramagnetic resonance studies. The most common solid salt of this ion is that of potassium (Fremy's salt). This salt is diamagnetic, is golden yellow, and is believed to contain the dimeric ion.

The most commonly used form of this ion is that of the potassium salt in aqueous solution, made alkaline to enhance the stability. The salts of tetraphenylarsonium and tetraphenylstibonium cations have been used in nonaqueous solutions in certain epr studies[2,3] and the solid tetraphenylstilbonium salt was reported used in one study as a polycrystalline mass.[4] No preparation, analysis, or purity information was reported. The free-radical ion has also been studied in solid potassium hydroxylamine disulfonate.[5]

We have succeeded in preparing a number of salts of this ion using cations larger than potassium. They are violet and are paramagnetic, with about one unpaired electron per anion. Epr properties of these salts are reported, along with the effects noted as the concentration of the free radical is changed.

Experimental Section

Preparation of Cesium Nitrosyldisulfonate.—A solution of the sodium salt was prepared by the method of Murib and Ritter.[6] This solution was saturated at room temperature with solid cesium chloride, after which it was filtered and cooled to 0°. The violet-blue needle-like crystals which formed were filtered off and recrystallized from 0.35 *N* cesium hydroxide at 50°. The crystals were washed with a small amount of cold water and then with absolute methanol, dried, and stored in a vacuum desiccator. These crystals gave no precipitate with a silver nitrate solution.

The salt was soluble in water, but insoluble in alcohol, acetone, nitromethane, and benzene. It is quite unstable and could be preserved in a vacuum desiccator for only a few hours.

This salt was analyzed by iodimetry. A few crystals of solid potassium iodide were added to an aqueous solution of the salt which was then acidified. The iodine produced by the reaction

$$H_3O^+ + ON(SO_3)_2^{2-} + I^- \longrightarrow 0.5I_2 + HON(SO_3)_2^{2-} + H_2O$$

gave the oxidizing equivalent weight 454; the calculated weight was 456. This purity (99.6%) was confirmed by determination of cesium by flame photometry and analysis of the colored anion by optical density measurements, using a Beckman DU spectrophotometer and the molar extinction coefficient of 20.8 at 545 mμ.[6]

Preparation of Tetraphenylarsonium Nitrosyldisulfonate.—Solid potassium nitrosyldisulfonate was added to a saturated aqueous solution of tetraphenylarsonium bromide, prepared by the method of Chatt and Mann.[7] The product precipitated on vigorous stirring. The suspension was cooled in ice water and filtered. The salt was washed with much cold water and then with anhydrous ether, dried, and stored in a vacuum desiccator. These crystals were quite insoluble in water and benzene but dissolved in chloroform, acetone, and similar solvents. Attempts at recrystallization resulted in considerable loss of product with no increase in purity, so in most preparations no recrystallization was attempted. This salt was quite stable if protected from moist air. A sample in an evacuated tube showed no change in magnetic susceptibility for well over 1 month.

Iodimetric determination was unsuited for this salt as the cation precipitates with triiodide ion. This suggested the alternate method of adding triiodide solution to a weighed sample to precipitate tetraphenylarsonium triiodide, which was collected on a filter, washed with water, dried at 100°, and weighed. This method indicated a purity of at least 99%. The most precise determination involved a potentiometric titration with ferrous

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