Sulfur Chelates. III.[1] Metal Complexes of the 1,1-Dithiolato Anions S_2CS^{2-}, S_2CNCN^{2-}, and $S_2CC(CN)_2^{2-}$

John P. Fackler, Jr., and D. Coucouvanis

Contribution from the Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106. *Received April 6, 1966*

Abstract: Anionic complexes of trithiocarbonate, CS_3^{2-}, N-cyanodithiocarbimate, S_2CNCN^{2-}, and 1,1-dicyanoethylene-2,2-dithiolate, $S_2CC(CN)_2^{2-}$, are described. These complexes are currently the most thoroughly studied members of a new general series of anionic complexes of the type $M(S_2C{=}X)_n^{z-}$, where z is the over-all charge and X is a wide variety of groups capable of forming a double bond with the carbon of the CS_2. The nickel(II), palladium(II), and platinum(II) complexes of these ligands show properties consistent with a planar MS_4 structure. The very interesting compound $[(n\text{-}C_3H_7)_4N]_2[Cu_4(i\text{-mnt})_3]$, with *i*-mnt being $S_2CC(CN)_2^{2-}$, is described. The compound is a 2:1 electrolyte in nitromethane and can be precipitated as the tetraphenylarsonium salt from acetone. It is suggested that the diamagnetic anion contains a tetrahedral cluster of copper(I) atoms with three equivalent *i*-mnt ligands. The electronic properties of $Cr(i\text{-mnt})_3^{3-}$ are shown to be consistent with an octahedral arrangement of sulfurs about the metal. The iron(III) and cobalt(III) complexes with *i*-mnt are isomorphous with the chromium(III) complex. Some additional complexes of *i*-mnt also are described and a correlation between the Δ_1 parameter of planar nickel(II) complexes and the Δ of octahedral chromium(III) complexes is presented.

In a recent communication[2] we described some properties of a new series of anionic complexes of general formula shown in Figure 1a, where X is an electron-withdrawing moiety and z is the charge on the complex. Complexes in the series have been made in which the atom in X bonded to the carbon is carbon, nitrogen, or sulfur. These complexes are formally related to the xanthates[3,4] (Figure 1b) and dithiocarbamates[3,5] (Figure 1c), but display some properties similar to those of the 1,2-dithiolato complexes (Figure 1d).[3,6]

Prior to our note, the only report of an anionic complex of a 1,1-dithiolate was the study by Deskin[7] of the formation constants of $Ni(S_2CS)_2^{2-}$. The complex was not isolated, however. Recently Werden, *et al.*,[8] have published their studies of the complexes formed with 1,1-dicyanoethylene-2,2-dithiolate (*i*-mnt); X = $C(CN)_2$ in Figure 1a. Investigating "the role of the ligand structure in stabilizing the $n = 0$ and -1 complexes," they[8] have reported the preparation and characterization of the *i*-mnt complexes of Ni(II), Pd(II), Pt(II), Cu(II), Au(III), Co(III), and Fe(III).

In this paper we wish to report the preparation and physical properties of trithiocarbonato complexes of nickel(II), palladium(II), and platinum(II), studies on the nickel(II), palladium(II), and platinum(II) complexes of N-cyanodithiocarbimate (S_2CNCN^{2-}), and our work on the complexes of 1,1-dicyanoethylene-2,2-dithiolate.

Experimental Section

Chemicals. All of the chemicals in this research were used as received. The products were washed with several portions of ether and were either air-dried or dried over anhydrous phosphorus(V) oxide *in vacuo*. Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Melting points recorded are uncorrected. The complexes have been checked for purity by thin layer chromatography.

Physical Measurements. The magnetic susceptibilities were determined at room temperature using the standard Gouy technique.[9] The calibrant was $Hg[Co(NCS)_4]$.[10]

Infrared spectra were obtained with a Beckman *IR*-8 recording spectrophotometer, the frequency being calibrated with polystyrene. Ultraviolet, visible, and near-infrared spectra were obtained with a Cary Model 14 recording spectrophotometer. Esr measurements were made on a Varian spectrometer.

Conductance measurements were made with a Leeds and Northrup conductivity bridge at room temperature.

The X-ray powder patterns of the complexes were observed with a Debye–Scherrer camera utilizing nickel-filtered copper radiation with λ 1.54050.

Polarographic measurements were performed using a commercial rotating platinum electrode and a Sargent Model XV polarograph. Dimethyl sulfoxide with a $LiClO_4$ supporting electrolyte was used with a saturated calomel electrode as reference.

Trithiocarbonate Complexes. Potassium Trithiocarbonate Solution. Carbon disulfide 10 ml (0.13 mole) was dissolved in 25 ml of dimethylformamide (DMF). A solution of 11.2 g (0.2 mole) of potassium hydroxide in 20 ml of water was added with stirring over a period of 5 min. About 50 ml of a blood red solution containing the trithiocarbonate anion, CS_3^{2-}, was obtained.

Dipotassium Trithiocarbonate. Solid dipotassium trithiocarbonate was prepared as described by Deskin.[7] The hygroscopic yellow crystals obtained gave complexes which are identical with the ones prepared from the above-described solution.

Bis(tetraphenylarsonium)bis(trithiocarbonato)nickel(II). To 10 ml of the DMF solution of CS_3^{2-} in 30 ml of 95% ethanol, 20 ml of a saturated (boiling ethanol) ethanolic nickel acetate solution was added after filtering. A deep red solution formed, along with ~2 g of a light green precipitate (presumably $Ni(OH)_2$). To the solution after filtration, 6 g of tetraphenylarsonium chloride in 50 ml of water was added and a red crystalline precipitate immediately formed. This precipitate was filtered, washed with cold ethanol (two 10-ml portions) and ether (five 10-ml portions) and air-dried; 3.9 g of crude product was recovered. The product was dissolved in hot nitromethane and ether was added until the first

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[1] For part I, see ref 2. This work was presented at the 152nd National Meeting of the American Chemical Society in Pittsburgh, Pa., March 1966.

[2] J. P. Fackler, Jr., and D. Coucouvanis, *Chem. Commun.*, 556 (1965).

[3] S. E. Livingstone, *Quart. Rev.* (London), 386 (1965).

[4] G. W. Watt and B. J. McCormick, *J. Inorg. Nucl. Chem.*, **27**, 898 (1965); *Spectrochim. Acta*, 21, 753 (1965).

[5] J. P. Fackler, Jr., and D. G. Holah, *Inorg. Nucl. Letters*, to be published, and references therein, especially M. Delepine, *Bull. Soc. Chim. France*, 5 (1958).

[6] A. H. Maki, T. E. Berry, A. Davison, R. H. Holm, and A. L. Balch, *J. Am. Chem. Soc.*, **88**, 1080 (1966), and references therein.

[7] W. A. Deskin, *ibid.*, 80, 5680 (1958).

[8] B. G. Werden, E. Billig, and H. B. Gray, *Inorg. Chem.*, **5**, 78 (1966).

[9] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 415.

[10] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

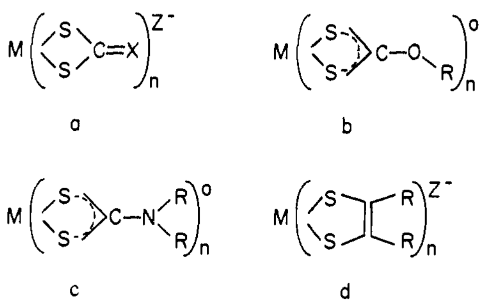

Figure 1. (a) 1,1-Dithiolato complexes. (b) Xanthate complexes. (c) Dithiocarbamate complexes. (d) Ethylene-1,2-dithiolato complexes.

cloudiness appeared. Upon cooling, 2.5 g of fine red needles was obtained, mp 217–218°.

Anal. Calcd for $C_{50}H_{40}As_2S_6Ni$: C, 57.30; H, 3.84. Found: C, 57.30; H, 3.86.

Bis(benzyltriphenylphosphonium)bis(trithiocarbonato)nickel(II). The benzyltriphenylphosphonium salt of the complex was prepared in a manner similar to that for the tetraphenylarsonium salt, mp 186–187°.

Bis(tetraphenylarsonium)bis(trithiocarbonato)platinum(II). To 15 ml of the ligand solution in 30 ml of 95% ethanol, a solution of 0.5 g of dipotassium tetrachloroplatinum(II), K_2PtCl_4, in 75 ml of ethanol–water (1:3) was added with stirring. The orange solution obtained was filtered into an aqueous solution (5 g in 70 ml of water) of tetraphenylarsonium chloride. An orange precipitate formed which was removed by filtration. The crude precipitate was recrystallized from nitromethane as described previously for the nickel(II) complex; 1.5 g of bright orange crystals was obtained, mp 244–245°.

Anal. Calcd for $C_{50}H_{40}As_2S_6Pt$: C, 46.80; H, 3.40. Found: C, 50.46; H, 3.63.

Bis(tetraphenylarsonium)bis(trithiocarbonato)palladium(II). The palladium complex was prepared from palladium dichloride, as bright yellow crystals, mp 224–225°, in a manner similar to that used for the platinum complex.

Anal. Calcd for $C_{50}H_{40}As_2S_6Pt$: C, 55.0; H, 3.66. Found: C, 54.5; H, 3.68.

Dipotassium N-Cyanodithiocarbimate (Cyanamide Dithiocarbonate).[11] The compound was prepared modifying Pera's synthesis.[12] Carbon disulfide, 7.6 g (0.1 mole), cyanamide, 4.2 g (0.1 mole), and potassium hydroxide, 11.2 g (0.2 mole), in 60 ml of water were put into a flask equipped with a reflux condenser and magnetic stirrer. The mixture was heated to 45° with stirring for 18 hr. A yellow solution containing the cyanodithiocarbimate (cdc) anion was obtained.

Bis(tetrapropylammonium)bis(N-cyanodithiocarbimato)nickel(II). To 10 ml of the aqueous solution diluted with 20 ml of water, 20 ml of a saturated (boiling water) aqueous nickel acetate solution was added. A dark green solution resulted. To this solution after filtration, 30 ml of a saturated (boiling water) aqueous solution of tetrapropylammonium iodide was added. The light green precipitate which formed was filtered off and dissolved in hot acetone. Water was added slowly until the first cloudiness appeared. Upon cooling, 5 g (90% based on cyanamide) of golden green plates was obtained, mp 220–221°.

Anal. Calcd for $C_{28}H_{56}N_6S_4Ni$: C, 50.70; H, 8.75; N, 12.67. Found: C, 50.82; H, 8.75; N, 12.54.

Bis(tetrapropylammonium)bis(N-cyanodithiocarbimato)palladium(II). The compound was prepared from dipotassium tetrachloropalladium(II) in a manner analogous to the method employed for the preparation of the nickel complex. Yellow crystals, mp 235–236°, were obtained.

Anal. Calcd for $C_{28}H_{56}N_6S_4Pd$: C, 47.3; H, 7.9; N, 11.9. Found: C, 46.9; H, 7.9; N, 11.8.

Bis(tetrapropylammonium)bis(N-cyanodithiocarbimato)platinum(II). The compound was prepared in a manner analogous to that used for the palladium(II) complex. Yellow needles, mp 224–226°, were obtained.

Anal. Calcd for $C_{28}H_{56}N_6S_4Pt$: C, 42.0; H, 7.0; N, 10.4. Found: C, 41.5; H, 7.0; N, 10.5.

Dipotassium 1,1-Dicyanoethylene-2,2-dithiolate. This compound, hereafter referred to as K_2(*i*-mnt), was prepared as indicated in the literature.[13]

Dipotassiumbis(*i*-mnt)nickel(II). Nickel acetate tetrahydrate, 2.46 g, was dissolved in 40 ml of 95% ethanol. The filtered solution was added to a solution of 4.36 g of the ligand in 20 ml of water, and the mixture was heated until all the precipitate dissolved. The solution was filtered, and on partial evaporation of the solvent under suction 3 g of yellow-green crystals was isolated, washed with ether (five 10-ml portions), and air-dried (60% yield), mp 350°.

Anal. Calcd for $C_8N_4S_4K_2Ni$: C, 23.02; H, 0.00; N, 13.42. Found: C, 23.16; H, 0.00; N, 13.43.

Bis(tetrapropylammonium)bis(*i*-mnt)nickel(II). The tetrapropylammonium salt of the complex was prepared in a manner analogous to that for the potassium salt. The product was recrystallized from an acetone–water (4:1) solution, washed with ether (five 10-ml portions), and dried. Brown-green crystals, mp 237–238°, were obtained.

Anal. Calcd for $C_{32}H_{56}N_6S_4Ni$: C, 54.10; H, 7.89; N, 11.80. Found: C, 54.27; H, 7.83; N, 11.41.

Bis(tetrapropylammonium)bis(*i*-mnt)palladium(II). Palladium(II) chloride, 0.1 g, was refluxed with 150 ml of ethanol for 15 min. The hot ethanolic solution was filtered into a solution of 0.5 g of K_2(*i*-mnt) and 0.5 g of tetrapropylammonium bromide in 40 ml of ethanol–water (1:1). The solution was boiled for 2 min, and upon cooling 0.3 g of yellow-golden crystals was isolated, mp 241–242°.

Anal. Calcd for $C_{32}H_{56}N_6S_4Pd$: C, 50.6; H, 7.4; N, 11.1. Found: C, 50.2; H, 7.5; N, 10.0.

Bis(tetrapropylammonium)bis(*i*-mnt)platinum(II). The platinum complex was prepared in a manner similar to the above from potassium tetrachloroplatinum(II) in 95% yield, using a minimum amount of water instead of ethanol. Yellow crystals, mp 241–242°, were produced.

Anal. Calcd for $C_{32}H_{56}N_6S_4Pt$: C, 45.2; H, 6.7; N, 9.6. Found: C, 45.3; H, 6.6; N, 9.9.

Bis(tetrapropylammonium)bis(*i*-mnt)copper(II). $CuSO_4 \cdot 5H_2O$, 2.50 g (0.01 mole), was dissolved in 100 ml of water with warming. To the filtered solution an equivalent amount (0.02 mole) of the cation halide solution was added.[14] The solution was heated near boiling and an aqueous solution of 5.3 g of K_2(*i*-mnt) in 75 ml of water was added while stirring. The reddish brown precipitate which formed was filtered off, redissolved in hot acetone, and crystallized by the addition of water until the solution first became cloudy. Cooling gave an ~70% yield of crystalline product, mp 209–210°.

Anal. Calcd for $C_{32}H_{56}N_6S_4Cu$: C, 53.5; H, 7.8; N, 11.6. Found: C, 53.7; H, 7.8; N, 11.7.

Bis(tetrabutylammonium)bis(*i*-mnt)copper(II). This complex, mp 173.4°, was prepared as for the tetrapropylammonium salt, starting with $[(n\text{-}C_4H_9)_4N]I$. The complex was reported recently by Werden, *et al.*,[8] to have mp 172–175° as prepared by a slightly different procedure.

Bis(tetrapropylammonium)tris(*i*-mnt)tetrakiscopper(I). Copper(II) bromide, 2.23 g (0.01 mole), in 100 ml of water, was added to an aqueous solution of 2.48 g (0.01 mole) of K_2(*i*-mnt) and 3.9 g (≃1.7 mole) of tetrapropylammonium bromide in 80 ml of water. A red-brown precipitate was formed which was recrystallized eight times from hot acetone by slowly adding water to first cloudiness and cooling. Orange-red crystals (2.5 g) which developed only one spot with thin layer chromatography were isolated, mp 261–262°.

Anal. Calcd for $C_{36}H_{56}N_8S_6Cu_4$: C, 41.4; H, 5.36; S, 18.4; N, 10.7; Cu, 24.2. Found: C, 41.12; H, 5.39; S, 18.2; N, 10.48; Cu, 23.8.[15]

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(11) The use of the name dithiocarbimate stems from the $>N{=}CS_2{}^{2-}$ linkage present and follows from the dithiocarbamate nomenclature for the $>N{-}CS_2{}^{-}$ linkage.

(12) J. D. Pera, U. S. Patent 2,816,136 (Dec 10, 1957); *Chem. Abstr.*, **52**, 5766*d* (1958).

(13) R. Gompper and W. Topfl, *Chem. Ber.*, **95**, 2851 (1962).

(14) Use of iodide salts gave some iodine and CuI(s) which reduced yields but otherwise did not seem to interfere. Often quaternary iodide salts are more readily available than the other halides.

(15) Copper(II) analysis using EDTA. Werden, *et al.*,[8] also report the formation of this product but do not characterize it.

Table I. Physical Properties of *i*-mnt, cdc, and CS_3 Complexes

Complex	Color	Λ ($10^{-3} M$)[b]	μ_{eff}^{cor},[a] BM	Complex	Color	Λ ($10^{-3} M$)[b]	μ_{eff}^{cor},[a] BM
$K_2Ni(i\text{-mnt})_2$	Green-brown	...	Diamag	$(Pr_4N)_3Fe(i\text{-mnt})_3$	Dark green	224	5.95
$(Pr_4N)_2Ni(i\text{-mnt})_2$	Brown-green	162	Diamag	$(Pr_4N)_3Mn(i\text{-mnt})_3$	Green	229	4.8[c]
$(BzPh_3P)_2Ni(i\text{-mnt})_2$	Light green	...	...	$(Pr_4N)_2Ni(cdc)_2$	Green	182	Diamag
$(Pr_4N)_2Pd(i\text{-mnt})_2$	Brown	175	...	$(Pr_4N)_2Pd(cdc)_2$	Yellow	178	...
$(Pr_4N)_2Pt(i\text{-mnt})_2$	Yellow	169	...	$(Pr_4N)_2Pt(cdc)_2$	Yellow	177	...
$(Pr_4N)_2Cu(i\text{-mnt})_2$	Brown-red	...	...	$(Ph_4As)_2Ni(CS_3)_2$	Red	171	Diamag
$(Bu_4N)_2Cu(i\text{-mnt})_2$	Brown-red	...[d]	...[d]	$(Ph_4As)_2Pd(CS_3)_2$	Brown-red	178	...
$(Pr_4N)_2Zn(i\text{-mnt})_2$	Pale yellow	164	...	$(Ph_4As)_2Pt(CS_3)_2$	Yellow-orange	176	...
$K_2Sn(i\text{-mnt})_3 \cdot 2H_2O$	Bright yellow	174	...	$(Pr_4N)_2Cu_4(i\text{-mnt})_3$	Yellow-orange	179	Diamag[e]
$(Pr_4N)_3Cr(i\text{-mnt})_3$	Green-brown	217	3.95	$(Ph_4As)_2Cu_4(i\text{-mnt})_3$	Yellow-orange	...	...

[a] Diamagnetic correction, ref 9, ~22°; Pr = $n\text{-}C_3H_7$, Bz = $C_6H_5CH_2$, Ph = C_6H_5, Bu = $n\text{-}C_4H_9$. [b] Nitromethane solvent at ~22°; 1:1 electrolyte, Λ ($10^{-3} M$) ~ 70–90 $ohm^{-1} cm^{-1}$; 2:1 electrolyte, Λ ($10^{-3} M$) ~ 160–180 $ohm^{-1} cm^{-1}$; 3:1 electrolyte, Λ ($10^{-3} M$) ~ 210–230 $ohm^{-1} cm^{-1}$. [c] Material slightly impure; see analysis. [d] Measurements reported in ref 8. [e] Also no esr signal could be found.

Table II. X-Ray Diffraction Data. *d* Spacings, A, of Some Strong Lines

Metal complex	*d* spacings						
$(Pr_4N)_2Ni(i\text{-mnt})_2$	10.43	9.55	8.12	6.95	5.37		
$(Pr_4N)_2Pt(i\text{-mnt})_2$	11.28	10.07	8.08	7.02	5.38		
$(Pr_4N)_2Zn(i\text{-mnt})_2$	15.03	12.90	10.03	9.17	7.64		
$(Pr_4N)_3Cr(i\text{-mnt})_3$	12.08	10.87	9.28	5.67	5.28		
$(Pr_4N)_3Fe(i\text{-mnt})_3$	11.90	10.90	9.39	5.70	5.28		
$(Pr_4N)_3Co(i\text{-mnt})_3$[a]	11.89	10.91	9.36	5.67	5.27		
$(Pr_4N)_3Mn(i\text{-mnt})_3$	11.33	9.51	6.46	5.98	4.79		
$(Ph_4As)_2Ni(CS_3)_2$	12.28	9.02	7.65	6.93	6.32	4.64	4.39
$(Ph_4As)_2Pd(CS_3)_2$	...[b]	9.12	...[b]	6.96	6.33	4.65	4.39
$(Ph_4As)_2Pt(CS_3)_2$	12.11	9.27	7.43	6.48	4.44		
$(Pr_4N)_2Ni(cdc)_2$	11.36	...[b]	7.86	6.81	5.61	4.70	
$(Pr_4N)_2Pd(cdc)_2$	11.32	8.68	7.90	6.88	5.69	4.81	
$(Pr_4N)_2Pt(cdc)_2$	11.36	...[b]	7.86	6.81	5.61	4.70	

[a] Chromium Kα radiation was used, Pr = $n\text{-}C_3H_7$, Ph = C_6H_5. [b] Weak, could not be read.

Bis(tetraphenylarsonium)tris(*i*-mnt)tetrakiscopper(I). By dissolving the tetrapropylammonium salt in acetone and adding an acetone–water solution of the quaternary arsonium chloride, the cation exchange occurs and the crystalline arsonium salt separates, mp 293–295°.

Anal. Calcd for $C_{60}H_{40}N_8S_6As_2Cu_4$: C, 49.79; H, 2.76; N, 5.80. Found: C, 49.93; H. 2.80; N, 5.83.

Bis(tetrapropylammonium)bis(*i*-mnt)zinc(II). The zinc complex was prepared in 80% yield from $ZnCl_2 \cdot 4H_2O$ using a procedure similar to that for the copper species. Pale yellow crystals, mp 146–147°, were obtained.

Anal. Calcd for $C_{32}H_{56}N_6S_4Zn$: C, 53.5; H, 7.8; N, 12.2. Found: C, 53.6; H, 7.9; N, 12.0.

Tris(tetrapropylammonium)tris(*i*-mnt)iron(III). The ferric complex was prepared in a manner analogous to that used for the copper complex, from ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$). The dark green crystals were recrystallized from acetone–water (4:1), mp 141–142°.

Anal. Calcd for $C_{48}H_{84}N_9S_6Fe$: C, 54.9; H, 7.9; N, 11.8. Found: C, 55.7; H, 8.1; N, 12.2.

Tris(tetrapropylammonium)tris(*i*-mnt)chromium(III). Anhydrous chromium(III) chloride, 1.3 g from $SOCl_2$ and $CrCl_3 \cdot 6H_2O$, was dissolved in 80 ml of absolute ethanol. The filtered solution was added to a solution of 3.3 g of $K_2(i\text{-mnt})$ and 3.9 g of tetrapropylammonium bromide in 40 ml of water. A green solution developed which was heated to near boiling. Water was added slowly until the first cloudiness appeared. On cooling, 3 g of brown-green crystals was recovered (yield 60%), mp 162–165°.

Anal. Calcd for $C_{48}H_{84}N_9S_6Cr$: C, 55.9; H, 8.1; N, 12.2. Found: C, 54.2; H, 8.0; N, 12.3.

Tris(tetrapropylammonium)tris(*i*-mnt)manganese(III). Manganese(II) acetate tetrahydrate, $Mn(CH_3CO_2)_2 \cdot 4H_2O$, 1.2 g (≃0.005 mole), was dissolved in 40 ml of water. To the aqueous Mn(II) solution, a hot solution of 3.30 g of $K_2(i\text{-mnt})$ and 3.9 g of tetrapropylammonium bromide in 40 ml of water was added with stirring.

A milky solution developed, along with a green oil that separated. To this mixture while heating, acetone (~100 ml) was added until a homogeneous green solution resulted. The solution was boiled for 1 min and filtered. On cooling for ~5 min an unidentified solid deposited which was filtered off. The remaining solution gave 1.5 g of green plates on partial evaporation (yield 30%), mp 148–150° (color change at 120°).

Anal. Calcd for $C_{48}H_{84}N_9S_6Mn$: C, 55.9; H, 8.1; N, 12.2. Found: C, 50.0; H, 7.6; N, 10.3.

Potassium Tris(*i*-mnt)tin(IV) Monohydrate. An aqueous solution of $K_2(i\text{-mnt})$ was mixed with aqueous tin(IV) chloride. The solution was warmed to ~60°, filtered, and allowed to cool to ~0°. Bright yellow crystals, mp 330° dec (yield approximately quantitative), were obtained.

Anal. Calcd for $C_{12}H_2N_6OSnK$: C, 22.7; H, 0.32; N, 13.2; H_2O, 2.8. Found: C, 22.7, 22.8; H, 0.57, 0.68; N, 13.2, 13.2; H_2O, 2.5.

Results

Table I summarizes the data characterizing the complexes reported in this paper. With bivalent metal ions, 2:1 electrolytes are obtained. The nickel(II) complexes in each case are diamagnetic and appear to be isomorphous from their X-ray powder patterns with the analogous palladium(II) and platinum(II) compounds (Table II).[16] With 1,1-dicyanoethylene-2,2-dithiol (*i*-mnt), the zinc(II) complex is not isomorphous with the nickel(II), palladium(II), platinum(II), or copper(II)[8] species. Anionic complexes of these latter ions presumably all are planar.[2,8] The $M(CS_3)_2^{2-}$ anions also undoubtedly are planar as is the coordination about the metal with the N-cyanodithiocarbimates.

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[16] $[(C_6H_5)_4As]_2Ni(CS_3)_2$ and $[(C_6H_5)_4As]_2Pd(CS_3)_2$ are isomorphous with each other but not with $[(C_6H_5)_4As]_2Pt(CS_3)_2$ even though the pattern for the latter complex is similar.

Table IIIA. Infrared Spectra (cm^{-1}) of *i*-mnt Complexes[a]

K_2(*i*-mnt)	K_2[Ni(*i*-mnt)$_2$]	$(Pr_4N)_2$-Ni(*i*-mnt)$_2$[c]	$(Pr_4N)_2$-Cu(*i*-mnt)$_2$	$(Pr_4N)_2$-Cu_4(*i*-mnt)$_3$	$(Pr_4N)_2$-Zn(*i*-mnt)$_2$	$(Pr_4N)_3$-Mn(*i*-mnt)$_3$	$(Pr_4N)_3$-Fe(*i*-mnt)$_3$[b]
		2960 (w)	2960 (w)	2960 (w)	2960 (w)	2960 (w)	2960 (w)
		2930 (w)	2930 (w)	2930 (w)	2930 (w)	2930 (w)	2930 (w)
		2900 (vw)	2900 (vw)	2900 (vw)	2900 (vw)	2900 (vw)	2900 (vw)
2200 (sh)	2265 (m)	2200 (s)	2200 (s)	2205 (s)	2200 (s)	2190 (sh)	2200 (s)
2195 (s)	2215 (s)				2185 (sh)	2200 (s)	
2100 (vw)	2150 (m)						
		1470 (m)	1470 (m)	1450 (m)	1465 (m)	1475 (m)	1465 (m)
	1405 (sh)	1400 (vs)	1400 (vs)	1400 (vs)			1392 (s)
1370 (w)	1380 (vw)	1380 (sh)	1390 (sh)				1365 (s)
	1260 (w)				1355 (s)	1340 (vs)	
1238 (m)		1235 (w)	1230 (w)	1220 (w)	1230 (s)	1230 (w)	1225 (w)
							1100 (vw)
		1040 (w)	1039 (w)	1040 (w)	1037 (w)		1037 (w)
987 (m)		981 (m)	982 (m)			1000 (w)	985 (sh)
					965 (s)	970 (m)	967 (m)
960 (s)	960 (sh)	968 (m)	965 (m)	970 (m)			
					953 (s)	950 (m)	940 (m)
	953 (m)	935 (m)	940 (m)		940 (m)		M
870 (s)	900 (s)[d]	890 (s)	895 (s)	915 (s)			
				855 (s)	880 (s)	880 (s)	883 (s)
		752 (m)	753 (m)[d]				
				757 (m)	867 (s)		845 (w)
					845 (w)	845 (w)	
					755 (m)	758 (m)[d]	755 (m)
		600 (s)		600 (s)	605 (m)		600 (w)
				545 (m)	520 (m)		475 (m)
		490 (sh)		490 (s)			
		475 (s)		470 (s)	495 (s)		415 (sh)
		378 (s)			480 (s)		370 (s)
					360 (s)		
		288 (m)			335 (s)		305 (w)

[a] KBr disks except for region below 600 cm^{-1} where Nujol mulls on polyethylene plates were used. [b] The chromium(III) and cobalt(III) complexes give nearly identical spectra with that of the iron(III) complex. [c] Pr = C_3H_7. [d] Spectrum not observed below 700 cm^{-1}.

The tris complexes of *i*-mnt are 3:1 electrolytes in nitromethane (Table I). Except for the cobalt(III) complex, they are all spin-free. The magnetic moment obtained for $(Pr_4N)_3$Fe(*i*-mnt)$_3$ agrees well with that reported by Werden, *et al.*[8] The manganese(III) complex is not isomorphous (Table II) with the others. Tris complexes with the other ligands were not readily prepared.

The preparation of 1,1-dithiolato complexes generally is readily accomplished starting with the sodium or potassium salt of the ligand. However, we have found that it is not necessary to first isolate the ligand salt since solutions containing this anion can be used directly. The reaction of CS_2 with a nucleophile in the presence of base is a very general one and, on addition of a metal salt along with the salt of a large cation to the resulting solutions, numerous new complexes can be prepared. To date over 20 different ligands have been used to give new complexes[2] of the type shown in Figure 1a. These complexes will be reported in subsequent papers.

Sometimes the addition of an appropriate cation has been found to be critical. With the complexes of CS_3^{2-}, for example, tetraalkylammonium salts could not be isolated. It appears that they are sufficiently soluble in the aqueous ethanol solution from which they are prepared to allow decomposition before crystallization. Little decomposition occurs when the crude product is rapidly precipitated with the tetraphenylarsonium cation. Studies have shown that the trithiocarbonates and some of the other complexes decompose in acid to form sulfur-rich complexes. With CS_3^{2-}, complexes of CS_4^{2-} are isolated, for example.

The preparation of the complex anion formulated as Cu_4(*i*-mnt)$_3^{2-}$ is interesting in that it is obtained during recrystallization of Cu(*i*-mnt)$_2^{2-}$ complexes[4] or in larger yields when bromide ion is present in the normal procedure for the preparation of the bis complex. The complex is diamagnetic, shows an infrared spectrum consistent with the presence of the cation and the *i*-mnt with no extraneous impurity, and is a 2:1 electrolyte in nitromethane based on the tetrameric copper(I) unit. The C–N stretch (Figure 2) is indicative of symmetric *i*-mnt. The total analysis of the tetrapropylammonium salt fits this formulation extremely well. Upon dissolving an analytical sample of the tetrapropylammonium salt in acetone and adding tetraphenylarsonium chloride in water–acetone, a crystalline compound is obtained which has been shown by its analysis and infrared spectrum to be identical with the tetrapropylammonium salt except that the original cations have been replaced by the tetraphenylarsonium cation. There is little doubt about the stoichiometry of this species.[17,17a]

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(17) The molecular weight of the tetrapropylammonium complex, 1200 at ~0.01 *M* concentration in acetone, also supports this result. The conductivity of the complex in acetone at ~0.01 *M* is only about 25% of the limiting value. The quantity of material used for the determination by Galbraith Laboratories is near the minimum limit for a meaningful molecular weight measurement.

(17a) NOTE ADDED IN PROOF. $(CH_3NPh_3)Cu_4$(*i*-mnt)$_3$ crystallizes with a = 15.42 A, b = 15.58 A, and c = 15.56 A, β^* = 84° 38′ in the space group $P2_1/n$. Assuming z = 4, the density calculated is 1.688 g/cm^3 (found 1.684 g/cm^3). This requires a molecular weight of 940. Based on the formula, the molecular weight is 946.

In Table III the infrared spectra of some of these complexes are reported.

Table IIIB. Infrared Spectra (cm^{-1}) of cdc Complexes[a]

$K_2(cdc)$[b]	$(Pr_4N)_2$-$Ni(cdc)_2$	$(Pr_4N)_2$-$Pd(cdc)_2$	$(Pr_4N)_2$-$Pt(cdc)_2$
2150 (s)	2185 (s)	2170 (s)	2180 (s)
	2125 (m)		
	1460 (s)	1460 (s)	1460 (s)
1320 (s)			1425 (vs)
	1425 (vs)	1425 (vs)	
1030 (s)	1040 (m)	1025 (m)	1025 (m)
	1028 (s)		
	989 (s)	983 (m)	985 (m)
970 (s)	972 (s)	962 (s)	960 (s)
	755 (s)	753 (m)	753 (m)
	578 (m)	578 (m)	565 (m)
	525 (m)	525 (m)	515 (s)
	512 (m)	512 (m)	
	380 (s)	374 (m)	378 (m)
		342 (s)	356 (m)
	350 (m)	322 (w)	308 (m)
		294 (m)	

[a] KBr disks except for region below 600 cm^{-1} where Nujol mulls on polyethylene plates were used. [b] Only prominent peaks are reported for the cdc compounds.

The absorption spectra of the *i*-mnt, cdc, and CS_3 complexes in acetonitrile are recorded in Table IV. For the *i*-mnt compounds, only those not reported by Werden, *et al.*,[8] are presented.

Polarography of these complexes generally shows irreversible oxidation which in the case of $Ni(CS_3)_2^{2-}$ is found to be dependent on the acid concentration of the solution. Chemical oxidation by iodine in some cases leads to new sulfur-rich species which can be isolated. We were not able to find an esr signal in $CHCl_3$–DMF (dimethylformamide) at room temperature or at 77°K for any solution containing an oxidation product. Vivid color changes do result during the oxidation, however. These properties will be described in detail when they have been characterized adequately. For the purpose of this paper it is sufficient to note that the oxidation appears to be more complicated than expected if the process simply involved a loss of an electron by the complex to form the -1 species.

Discussion

Structures. The complexes of the planar tetranuclear anion CS_3^{2-} are the simplest sulfur chelate complexes that have been heretofore isolated. The $M(S_2CS)_2^{2-}$ anions formed with nickel(II), palladium(II), and platinum(II) contain four fewer nuclei than the very interesting $M(S_2C_2H_2)_2^{2-}$ complexes reported by Schrauzer and Mayweg.[18] Like the complexes of ethylene-1,2-dithiol, the CS_3^{2-} complexes of nickel(II), palladium(II), and platinum(II) are undoubtedly planar. The infrared spectra (*vide infra*) clearly show the presence of the expected C=S stretch near ~1000 cm^{-1}. Krebs[19] and Gatton recently reported the X-ray crystal structure of $(HS)_2CS$ at $-100°$ which shows the CS_3 group to be planar. Two groups[20,21] have discussed the infrared spectrum and structure of the CS_3^{2-} anion itself.

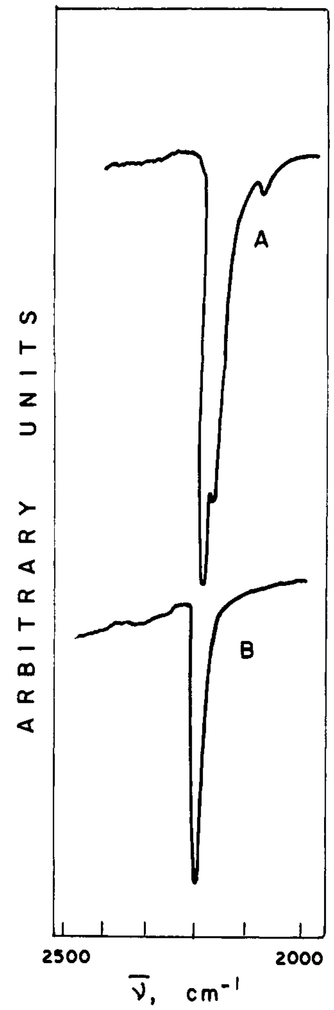

Figure 2. CN stretching region for (A) $(Pr_4N)_3Mn(i\text{-mnt})_3$ and (B) $(Pr_4N)_2Cu_4(i\text{-mnt})_3$.

The complexes of N-cyanodithiocarbimate with nickel(II), palladium(II), and platinum(II) contain a square-planar arrangement of sulfurs about the metal ion. It was necessary to consider the possibility that the structure of the complex was different from that of Figure 1a since the CN nitrogen might participate in coordination to the metal. However, the infrared stretch of the C≡N group, 2170–2185 cm^{-1}, in the three complexes and the absence of a strong C=S stretch (*vide infra*) suggested normal sulfur coordination. Professor Cotton[22a] has informed us that he and J. McCleverty have prepared several complexes of this ligand and that preliminary results of an X-ray investigation of the nickel(II) complex[22b] show the anion to be planar and bonded as we have indicated[2] previously.

Complexes of *i*-mnt with the bivalent ions nickel(II), palladium(II), platinum(II), and copper(II) are square-planar.[23]

(18) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).

(19) B. Krebs and G. Gatton, *Z. Anorg. Allgem. Chem.*, **340**, 294 (1965).

(20) A. Fadini, A. Müller, and B. Krebs, *Z. Naturforsch.*, **20a**, 1241 (1965).

(21) H. Seidel, *Naturwiss.*, **52**, 257 (1965).

(22) (a) F. A. Cotton, private communication; (b) C. Harris and F. A. Cotton, private communication.

(23) See the discussion in ref 8 and 34.

Table IV. Electronic Spectra of *i*-mnt, cdc, and CS_3 Complexes in Acetonitrile

ν_{max}, cm^{-1}	ϵ, l. mole^{-1} cm^{-1}	$\bar{\nu}_{max}$, cm^{-1}	ϵ, l. mole^{-1} cm^{-1}	$\bar{\nu}_{max}$, cm^{-1}	ϵ, l. mole^{-1} cm^{-1}
$Cr(i\text{-mnt})_3{}^{3-}$ [a]		$Pt(CS_3)_2{}^{2-}$		$Pt(cdc)_2{}^{2-}$	
15,150	36	21,000 (sh)	400	24,600	4×10^3
20,250 (sh)	50	23,200	3.6×10^3	27,400	2.8×10^4
22,700 (sh)	227	27,200	316	31,000 (sh)	3.3×10^3
26,800	7.2×10^3	30,500	700	34,500	1.4×10^4
30,500	5.2×10^3	24,000 (sh)	2.0×10^3	38,500	4.6×10^4
35,700	2.6×10^3	37,000	3.8×10^3	45,500	2.3×10^4
42,500	2.5×10^3	38,000	7.9×10^3		
$Ni(cdc)_2{}^{2-}$		$Zn(i\text{-mnt})_2{}^{2-}$		$Pd(CS_3)_2{}^{2-}$	
15,900[b]	80	29,400	5.8×10^3	23,000 (sh)	3.6×10^2
18,200 (sh)[b]	$\simeq 60$	33,150	2.60×10^3	25,600	1.9×10^3
20,200 (sh)	194	42,400	7.9×10^2	30,300	4.0×10^3
22,500 (br sh)	1.9×10^3			34,000 (sh)	2.2×10^3
24,700[b]	1.1×10^4			37,000	1.5×10^3
30,800	4.0×10^4			38,000	1.8×10^3
39,000	3.3×10^4				
$Ni(CS_3)_2{}^{2-}$		$Pd(cdc)_2{}^{2-}$			
16,400 (sh)[b]	$(\simeq 15)$	22,500	270		
18,400[b]	(120)	24,000 (sh)	224		
19,800[b]	(1000)	28,200	7.2×10^3		
21,700 (sh)	4.4×10^2	30,600	3.5×10^4		
30,600	(4.3×10^3)	32,700	5.4×10^4		
37,000	2.7×10^3	41,800	2.4×10^4		
38,000	1.94×10^3				

[a] Spectrum identical in cyclohexanone and pyridine. [b] Positions independent of solvent, cyclohexanone and pyridine.

With trivalent ions, it is possible that the sulfurs may be arranged in either a trigonal-prismatic or an octahedral configuration. The visible spectrum (*vide infra*) of $Cr(i\text{-mnt})_3{}^{3-}$ (this complex is isomorphous with the iron(III) and cobalt(III) complexes) suggests strongly that these compounds have the octahedral structure of six sulfurs about the metal. The only compound in this series which may be different is the $Mn(i\text{-mnt})_3{}^{3-}$ anion since the tetrapropylammonium salt is not isomorphous with the other tris *i*-mnt complexes.

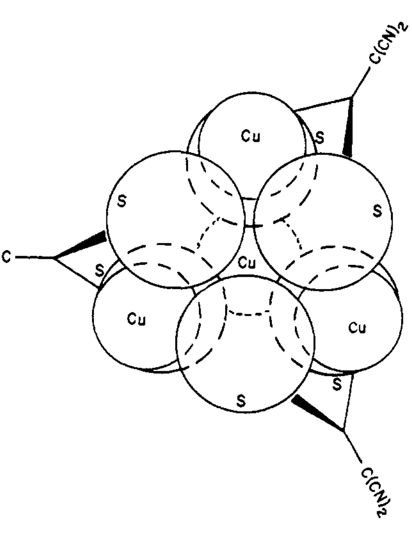

Figure 3. Proposed structure for $Cu_4(i\text{-mnt})_3{}^{2-}$.

If correctly formulated, the unusual anion $Cu_4(i\text{-mnt})_3{}^{2-}$ is the first example of an ionic copper cluster compound. However, ionic cluster compounds are common with other elements.[24,25] The rather uncomplicated infrared spectrum (Table III) suggests that the anion is highly symmetrical. A cluster with sulfur ligands and copper(I) has been reported by Hesse[26] for the copper(I) diethyldithiocarbamate. In $Cu_4(dtc)_4$, the copper(I) atoms are arranged in a tetrahedron with a sulfur atom from each dithiocarbamate bridging the copper atoms. The copper(I) atoms have three nearest neighbor sulfur atoms but the coordination is of necessity somewhat irregular. It has been noted[26] that $[(C_2H_5)_3AsCuI]_4$ also has copper(I) atoms at the corners of a tetrahedron.[27] The Cu-Cu distances in $Cu_4(dtc)_4$ are 2.76 and 2.66 A, only 0.1-0.2 A longer than in the metal.[26]

While several possible structures for the $Cu_4(i\text{-mnt})_3{}^{2-}$ anion can be imagined if one allows an indiscriminate coordination of the metal with the sulfur, it seems very likely that each copper atom is coordinated by two or more sulfur atoms and that a tetrahedral Cu_4 cluster is present. A simple, rather symmetric arrangement can be constructed (Figure 3) which satisfies these requirements and agrees well with the physical data obtained.

In the structure of Figure 3, each of the six sulfur atoms occupies a face of a cube with copper(I) atoms at alternate corners. Thus the sulfur atoms are arranged in an octahedron, giving a propeller-like D_3 symmetry to the complex as a whole. The copper(I) atoms occupy four of the trigonal holes. In this structure the copper(I) atom on the threefold axis is symmetrically different from the other three. Each sulfur atom in this structure is bonded to two nearest neighbor copper(I)

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[24] J. Lewis, *Pure Appl. Chem.*, 10, 11 (1965).

[25] J. H. Espenson and R. E. McCarley, *J. Am. Chem. Soc.*, **88**, 1063 (1966), and references therein.

[26] R. Hesse, *Arkiv Kemi*, 20, 481 (1962).

[27] R. E. Rundle and J. H. Sturdivant, *J. Am. Chem. Soc.*, 69, 1561 (1947).

Table V. Infrared Spectra of the Trithiocarbonato Anions

CS_3^{2-} [a]	$BaCS_3$ [b]	$Ni(CS_3)_2^{2-}$	$Pd(CS_3)_2^{2-}$	$Pt(CS_3)_2^{2-}$	Assignment
	943	1010 (s)	1015 (s)	1025 (s)	C=S
	912	1000 (s)	1005 (s)	1010 (s)	Stretch
905 (ν_3)					E′ asym stretch
	835	843 (br)	845 (m)	855 (m)	C—S stretch and (?)
	836		835 (m)	830 (m)	$\nu_2 + \nu_4$ combination
520 (ν_1)					A′ sym stretch
505 (ν_2)	518	505 (w)	500 (w)	. . .	A_2'' deformation (?)
320 (ν_4)	330	380	360 (?)	. . .	E′ bend and
	321	. . .	. . .	. . .	M—S stretch

[a] Reference 20; s = strong, w = weak, br = broad, m = medium. [b] Reference 21.

atoms and each copper(I) is coordinated with three sulfur atoms, a reasonable coordination for both species.

Infrared Spectra. The infrared spectra of the trithiocarbonato complexes show bands associated with the anions at ~1000, ~840, ~500, and 350–380 cm^{-1} (Table V). Fadini, *et al.*,[20] recently reported the results of a normal coordinate analysis of the CS_3^{2-} anion which resulted in the assignments given in the table. The stretching vibrations ν_1 and ν_3 are shifted somewhat in the complexes, and ν_3, the doubly degenerate asymmetric stretch, is split into two components. Rather than label the 835 and 826-cm^{-1} bands in $BaCS_3$ with Seidel[21] as "$\nu_1 + \nu_4$ combinations," it seems to us that one of these bands is a C–S stretch while the other may be a $\nu_2 + \nu_4$ combination. The presence of the metal ion reduces the symmetry of the CS_3^{2-} unit to C_{2v} which should generate three dipole-allowed C–S stretching modes. The strong C=S stretching band near 1000 cm^{-1} is found also in thioketones[28] and in ethylene trithiocarbonate.[28]

The increase in the C–S single bond frequency from the 600 to 700 cm^{-1} region in which it generally is found[28] may result from a C–S bond order increased somewhat above one by contributions of resonance structures which place partial positive charge on the coordinated sulfurs and by kinematic coupling with the metal. The metal–sulfur stretch at ~380 cm^{-1} in $Ni(CS_3)_2^{2-}$ agrees well with the M–S stretch reported by Nakamoto[29] for the dithioxalato complex.

The features of importance to be noted in the infrared spectra of the *i*-mnt and cdc complexes are the C–N stretches near 2100 cm^{-1} and the C–S stretches near 880 cm^{-1}. For the *i*-mnt complexes of Ni(II), Pd(II), Pt(II), Cu(II), as well as for the tris complexes of Fe(III), Co(III), and Cr(III), the C–N stretch appears at 2200 ± 5 cm^{-1} and is not split; but with Zn(*i*-mnt)$_2^{2-}$ and Mn(*i*-mnt)$_3^{3-}$ definite splittings of this peak are observed. The splittings may reflect a lower symmetry for these complexes than for the analogous complexes with bivalent or trivalent metals. The lack of isomorphism of the X-ray powder patterns of zinc with the other bivalent metal ions and manganese(III) with the trivalent metal ions is consistent with this possibility. The sharp single band observed for the C–N stretch in Cu$_4$(*i*-mnt)$_3^{2-}$ is particularly significant and does agree with the symmetry proposed for the anion. The C–N stretch in the cdc complexes falls from 2170 to 2185 cm^{-1} and is at 20–30 cm^{-1} higher frequency than in the free cdc anion itself. A slight but apparently real increase occurs in the C–S stretch in the order Co > Cr > Fe > Mn for the tris *i*-mnt complexes.

Electronic Structures. The electronic properties of the planar *i*-mnt complexes have been discussed adequately by Werden, *et al.*[8] It should be pointed out, however, that while resonance structures of the type possible with the 1,2-dithiolato complexes are not permitted with 1,1-dithiolato complexes, there is substantial evidence for short-lived oxidation products with most of the 1,1-dithiolato complexes including those reported here and with certain ones stable oxidized species may be obtained. The oxidation often is followed by a decomposition to some new species. These oxidations will be described in another communication.

Assuming with Gray and Ballhausen[30] that the square-planar *i*-mnt, cdc, and CS_3 complexes of nickel(II) have a $^1A_g[\ldots(\sigma^*,d_{x^2-y^2})^2]$ ground state in D_{2h} symmetry, the lowest energy transition reflects the ligand field strength of the complex. Correcting the energy separation $^1A_g \rightarrow {}^1B_{1g}(d_{x^2-y^2} \rightarrow d_{xy})$ for electron repulsions and assuming with Werden, *et al.*,[8] a reasonable value for the Slater–Condon parameters, Table VI is constructed.[31,32] The new complexes of nickel(II) reported in this work have the largest Δ_1^{Ni} parameters so far observed for sulfur chelate complexes with a four-membered ring.

The consistency of the electronic spectral results for the 1,1-dithiolato complexes of nickel(II) and chromium(III) with the wide variety of sulfur ligands and the typical octahedral spectrum that is observed for Cr(*i*-mnt)$_3^{3-}$ indicate (1) that the $^1A_g \rightarrow {}^1B_{1g}$ indeed is the lowest observed transition[33] in the nickel(II) complexes, and (2) the tris complexes have an octahedral rather than a trigonal prismatic sulfur arrangement about the metal. Since the Δ_1^{Ni} parameter for the planar nickel(II) complexes[34] reflects the ligand field strength, it can be assumed that the ratio $\Delta_1^{Ni}/\Delta^{Cr}$, where Δ^{Cr} is the ligand-field splitting parameter for the chromium(III) complex, will be nearly constant for a variety of ligands. Calculating this ratio from the lowest

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[28] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956, p 356.

[29] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 214.

[30] H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

[31] C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

[32] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 235.

[33] This analysis also requires the absence of solvent perturbations.

[34] H. B. Gray, *Progr. Transition Metal Chem.*, **1**, 239 (1965).

energy spin-allowed transition observed[31] with $Cr(dtp)_3$ and the Δ_1^{Ni} for $Ni(dtp)_2$,[8] $\Delta_1^{Ni}/\Delta^{Cr} = 1.21$ is obtained. The $^4A_g \rightarrow {}^4T_{2g}$ and $^4A_g \rightarrow {}^4T_{1g}$ transitions in other chromium(III) complexes were calculated from this ratio using the electronic repulsion parameters given. The agreement is extremely good (Table VI).

Table VI. Electronic Parameters for 1,1-Dithiolato Complexes[a]

Complex	Ring	Δ_1^{Ni}, cm^{-1}	$^1A_g \longrightarrow {}^1B_{1g}$
$Ni(mnt)_2^{2-}$	MS_2C_2	14,500	11,700[b]
$Ni(dtp)_2$	MS_2P	17,300	14,500[c]
$Ni(S_2CNH_2)_2$	MS_2C	18,400	15,600[c]
$Ni(i\text{-mnt})_2^{2-}$	MS_2C	18,500	15,700
$Ni(dtc)_2$	MS_2C	18,600	15,800[c]
$Ni(cdc)_2^{2-}$	MS_2C	18,670	15,870
$Ni(cad)_2^{2-}$	MS_2C	18,800	16,000[d]
$Ni(CS_3)_2^{2-}$	MS_2C	19,200	16,400
$Ni(ced)_2^{2-}$	MS_2C	19,500	16,700[d]

Complex	$^4A_g \longrightarrow {}^4T_{2g}$ Calcd[e]	Obsd	$^4A_g \longrightarrow {}^4T_{2g}$ Calcd[e]	Obsd[f]
$Cr(dtp)_3$	14,300[e]	14,300[e,c]	19,100	18,100 (?)
$Cr(S_2CNH_2)_3$	15,200	15,500[c]	20,000	20,000
$Cr(i\text{-nmt})_3^{3-}$	15,300	15,100	20,100	20,250
$Cr(dtc)_3$	15,370	15,500[c]	20,170	20,400
$Cr(cad)_2^{3-}$	15,540	15,400[d]	20,340	19,400 (?)[d]
$Cr(ced)_3^{3-}$	16,120	16,260[d]	20,920	22,730 (?)[d]

[a] $F_2 = 10F_4 = 800$ cm^{-1} for Cr(III) and Ni(II). [b] Reference 8, mnt = 1,2-dicyanoethylene-1,2-dithiolate. [c] Reference 31, dtc = diethyldithiocarbamate, dtp = $S_2P(OC_2H_5)_2$. [d] Compounds currently under investigation; cad = $S_2CC(CN)C(O)NH_2$ and ced = $S_2CC(CN)COOC_2H_5$. [e] Data used to calculate $\Delta_1^{Ni}/\Delta^{Cr}$ ratio of 1.21. [f] Charge-transfer bands cause this absorption to appear as a shoulder which is not well defined in some of the complexes.

Agreement between the calculated and observed transitions for the chromium(III) complexes based on the lowest energy transition in the nickel(II) complexes is quite unlikely if the lowest energy nickel(II) transition does not reflect the separation between the d_{xy} and $d_{x^2-y^2}$ orbitals. Only this transition in planar nickel(II) complexes is independent of the tetragonality of the complex. Furthermore, the agreement should be good only for octahedral chromium(III) complexes since the lowest energy transition in this symmetry is a $t_{2g} \rightarrow e_g$ ($\Delta = 10Dq$) transition. With the same $\Delta_1^{Ni}/\Delta^{Cr}$ ratio, surprisingly good results are obtained for the β-ketoenolato complexes assuming the 18,700-cm^{-1} band in the dipivaloylmethane complex[35] of nickel(II) contains the Δ_1^{Ni} transition. This leads to a Δ^{Cr} for the chromium(III) complex of 17,950 which is to be compared with the transition in the acetylacetonate[35] which is found at 17,500 cm^{-1}.

The fit we observe for the xanthate and cyanide complexes deserves some comment. With $Cr(S_2COC_2H_5)_3$, the $^4A_g \rightarrow {}^4T_{2g}$ transition appears at 16,130 cm^{-1} while it is calculated to appear at 15,100 cm^{-1} using the Δ_1^{Ni} reported by Werden, *et al.*[8] This may mean the assignment in the Ni(xanthate)$_2$ is incorrect or the chromium(III) complex is not octahedral.[36] This structure is not known.

With $Ni(CN)_4^{2-}$, Gray and Ballhausen[30] report Δ_1^{Ni} to be 24,950 cm^{-1}. Thus a band at 20,600 cm^{-1} is expected in $Cr(CN)_6^{3-}$ using the same $\Delta_1^{Ni}/\Delta^{Cr}$ ratio of 1.21. The lowest energy band observed[37] in $Cr(CN)_6^{3-}$ appears at 26,600 cm^{-1}. However, assuming with Perumareddi, Liehr, and Adamson[38] that the $^1A_{1g} \rightarrow {}^1A_{2g}$ (D_{4h}, $d_{xy} \rightarrow d_{x^2-y^2}$) transition in $Ni(CN)_4^{2-}$ appears at 28,010 cm^{-1}, the band in the chromium complex should fall near 25,500 cm^{-1}. Recently Ballhausen, *et al.*,[39] have examined the polarized spectrum of $Ni(CN)_4^{2-}$. Assuming a Δ_1^{Ni} value of 34,000 cm^{-1} with $F_2 = 10F_4 = 1000$ cm^{-1} and $\Delta_2^{Ni} = 0$, they assign a band near 23,000 cm^{-1} to the $^1A_{1g} \rightarrow {}^1B_2$ transition while the transition $^1A_{1g} \rightarrow {}^1A_{2g}$ is placed near 30,500 cm^{-1} "probably covered by charge-transfer bands." Using the data for $Cr(CN)_6^{3-}$ to calculate Δ_1^{Ni} by our procedure, the transition $^1A_{1g} \rightarrow {}^1A_{2g}$ should appear at ~29,400 cm^{-1}. This result clearly supports the placing[38,39] of the transition $^1A_{1g} \rightarrow {}^1A_{2g}$ in the ~30,000-cm^{-1} region.

Since the $Cr(i\text{-mnt})_3^{3-}$ is very likely octahedral (D_3) the isomorphous iron(III) and cobalt(III) complexes must have similar structures. The trigonal prismatic configuration for the mnt complexes has not been established with certainty but we have been informed[40] that the spectrum of $Cr(mnt)_3^{3-}$ is considerably different from that of our $Cr(i\text{-mnt})_3^{3-}$.[41] It is apparent that any differences in the electronic and structural properties of the isoelectronic mnt and *i*-mnt complexes must result from the delocalized π system only possible in the 1,2-dithiolato complexes. Assuming reasonable bond angles (120°) and C–S bond distances (1.81 A), the S···S "bite" distance in the *i*-mnt ligand is estimated to be very nearly the same as the bite distance[33] in $Ni(mnt)_2^{2-}$. Size relationships alone would predict *i*-mnt and mnt complexes to be similar.

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(35) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, in press.

(36) Or the relationship breaks down. We suspect, however, that the lowest transition in the nickel complex is not the $d_{x^2-y^2} \longrightarrow d_{yx}$ transition.

(37) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding," Addison-Wesley Publishing Co., Reading, Mass., 1962, p 291.

(38) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 259 (1963).

(39) C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, **4**, 514 (1965).

(40) H. B. Gray, California Institute of Technology, private communication.

(41) NOTE ADDED IN PROOF. A recent note by R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 2874 (1966), suggests $VL_3^{2-,3-}$ species may have structures close to idealized octahedra rather than trigonalpr ismatic like $V(S_2C_2Ph_2)_3$. If $Cr(mnt)_3^{3-}$ is octahedral, the spectral data for $Ni(mnt)_2^{2-}$ predict bands will be found at 12,000 and 16,800 cm^{-1}.