compounds $Fe_2Cp_3^+$ and $Ni_2Cp_3^+$.[6] We are currently investigating the possibility of similar europium compounds. After this article was prepared, another report on Yb_2Cp_4 appeared.[7] Although our results differ in some areas, the gross features are substantially the same.

Experimental Section

The compounds were prepared on a vacuum line by transferring some 30 ml of anhydrous ammonia and 0.04 mol of cyclopentadiene to a vessel containing 0.01 g-atom of Yb metal (99.9%). The vessel was subsequently warmed with a chloroform slush in order to liquefy the ammonia. After 2 hr, NH_3 and excess cyclopentadiene were removed and the products were obtained by fractional sublimation. Owing to the ease of oxidation and hydrolysis of these compounds, rigid exclusion of oxygen and moisture was necessary throughout their preparation and examination. Nmr analyses were performed on a Varian A-60A and a Picker MS 902 was used for mass spectral analysis. The vanishing-current method was used for appearance potential measurements and xenon was used as a reference.

Acknowledgment.—The partial support of this work by the National Science Foundation (Grant No. GP-7881) is gratefully acknowledged.

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Complexes of Cationic Dithiocarbamate Ligands

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Complexes of cationic ligands have been reported infrequently, although the few reports available suggest that such compounds may be stable and amenable to detailed study. Quagliano and coworkers[1-3] have recently characterized a variety of complexes derived from positively charged diamine and zwitterion ligands and Meek[4] has reported the first example of coordination by a positively charged phosphorus ligand.

We report here the preparation and characterization of several dithiocarbamate complexes of cobalt(III), nickel(II), and palladium(II), some of which are highly charged and involve cationic ligands.

Experimental Section

Reagents.—Reagent grade metal salts and 1,1,7,7-tetraethyldiethylenetriamine (Ames Laboratories, Inc.) were used as received. The yellowish white compound N,N-di(2-N,N-diethylamino)ethyldithiocarbamic acid (L) was prepared by treating 1,1,7,7-tetraethyldiethylenetriamine with carbon disulfide in diethyl ether.[5,6] The ammonium and potassium salts of N,N-di(2-N,N-diethylamino)ethyldithiocarbamate (L^-) were prepared by treating L with NH_4OH and KOH, respectively, in methanol. Other reagent grade materials were used as received.

Preparation of Complexes. Bis(N,N-di(2-N,N-diethylamino)ethyldithiocarbamato)nickel(II), $Ni(L^-)_2$.—An aqueous solution of 2.37 g (0.01 mol) of $NiCl_2 \cdot 6H_2O$ in 50 ml of water was treated with 50 ml of water containing 6.60 g (0.02 mol) of potassium N,N-di(2-N,N-diethylamino)ethyldithiocarbamate. The green complex which formed was separated by filtration, washed with water, and dried *in vacuo* over P_4O_{10}. The compound was diamagnetic. *Anal.* Calcd for $C_{26}H_{56}N_6NiS_4$: C, 48.8; H, 8.83; N, 13.1. Found: C, 49.0: H, 8.84; N, 13.1.

Bis(N,N-di(2-N,N-diethylamino)ethyldithiocarbamato)palladium(II), $Pd(L^-)_2$.—A solution of 0.978 g (0.003 mol) of K_2PdCl_4 in 30 ml of water was added slowly to 1.85 g (0.006 mol) of ammonium N,N-di(2-N,N-diethylamino)ethyldithiocarbamate. The yellow precipitate which formed was collected on a filter and washed with water. Recrystallization from methanol by slow addition of water followed by drying *in vacuo* over P_4O_{10} provided an analytically pure sample. *Anal.* Calcd for $C_{26}H_{56}N_6PdS_4$: C, 45.4; H, 8.20; N, 12.3. Found: C, 45.6; H, 8.39; N, 12.3.

Tris(N,N-di(2-N,N-diethylamino)ethyldithiocarbamato)cobalt(III), $Co(L^-)_3$.—To 8.25 g (0.025 mol) of potassium N,N-di(2-N,N-diethylamino)ethyldithiocarbamate was added 2.14 g (0.008 mol) of hexaamminecobalt(III) chloride in 200 ml of water. The resulting mixture was heated at 80° for 30 min during which time ammonia was evolved and a dark green, tacky oil collected at the bottom of the container. The oil was separated from the reaction solvent and dissolved in ether. After filtration the ether was evaporated to leave a green oil which could not be crystallized. Elemental analyses were not obtained for the oil; however, the optical and infrared spectra and chemical properties indicated that the compound is a tris(dithiocarbamato)cobalt(III) complex.[7,8]

Bis(N,N-di(2-N,N-diethylammonium)ethyldithiocarbamato)nickel(II) Chloride, $Ni(L^+)_2Cl_4$. Method 1.—To 1.46 g (0.005 mol) of L in 50 ml of methanol was added 5.0 ml of 1 *M* (0.005 mol) hydrochloric acid. This produced the positively charged ligand L^+ in solution. To this solution was added 0.594 g (0.0025 mol) of $NiCl_2 \cdot 6H_2O$ in 20 ml of methanol, whereupon the green complex $Ni(L^+)_2Cl_4$ formed. Addition of diethyl ether resulted in the precipitation of solid, green $Ni(L^+)_2Cl_4$ which was identical with that prepared by method 2.

Method 2.—Dry hydrogen chloride was bubbled into a solution of $Ni(L^-)_2$ in diethyl ether. Green microcrystals of $Ni(L^+)_2Cl_4$ began to form immediately and after *ca.* 5 min the crystals were collected on a filter, washed with 60 ml of cold HCl-saturated ether, air dried, and then dried *in vacuo* over P_4O_{10}. The compound was diamagnetic. In practice, method 1 was less convenient than method 2 and most of the samples studied in this work were prepared by the latter procedure. *Anal.* Calcd for $C_{26}H_{60}Cl_4N_6NiS_4$: C, 39.8; H, 7.70; Cl, 18.0; N, 10.7. Found: C, 39.7; H, 7.89; Cl, 17.6; N, 10.5.

Bis(N,N-di(2-N,N-diethylammonium)ethyldithiocarbamato)palladium(II) Chloride, $Pd(L^+)_2Cl_4$. Method 1.—This method was analogous to that given above for $Ni(L^+)_2Cl_4$. The starting palladium compound was K_2PdCl_4.

Method 2.—This procedure corresponded to method 2 given above for the preparation of $Ni(L^+)_2Cl_4$. *Anal.* Calcd for $C_{26}H_{60}Cl_4N_6PdS_4$: C, 37.3; H, 7.25; Cl, 16.5. Found: C, 37.4; H, 7.25; Cl, 16.0.

Tris(N,N-di(2-N,N-diethylammonium)ethyldithiocarbamato)cobalt(III) Chloride, $Co(L^+)_3Cl_6$.—Approximately 3 g (0.0035

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(8) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemistilehti*, **B29**, 75 (1956).

mol) of $Co(L^-)_3$ was treated with 4 ml of 6 *M* (0.024 mol) hydrochloric acid and 8 ml of ethanol. After 15 min the oil had dissolved to give a green solution to which was added slowly and with stirring 50 ml of HCl-saturated ether. The green microcrystalline product which separated was washed with HCl-saturated ether, air dried, and then dried *in vacuo* over P_4O_{10}. *Anal.* Calcd for $C_{39}H_{90}Cl_6CoN_9S_6$: C, 40.8; H, 7.90; Cl, 18.5. Found: C, 40.8; H, 8.11; Cl, 18.8.

Measurements.—Infrared spectra were recorded with a Beckman IR-8 spectrometer on both Nujol mulls and KBr disks. Electronic spectra were measured in 10-mm matched quartz cells with a Cary Model 14 spectrophotometer. Conductivities were determined for 10^{-3} *M* solutions with a Beckman RC-18 conductivity bridge at 25°. Analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. Pertinent data are given in Table I.

TABLE I

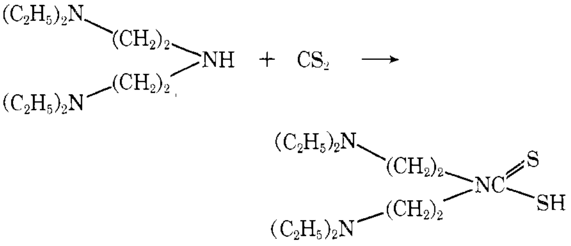
PROPERTIES OF DITHIOCARBAMATE COMPLEXES[a]

Compound	$\bar{\nu}$(C═N)	$\bar{\nu}(N—H^+)$[b]	E_{max} (ε)[c]	Λ_M[d]	Mp, °C
$Co(L^-)_3$	1.490	...	15.5 20.7[g] 25.3[g] 30.8	[e]	Oil
$Ni(L^-)_2$	1.505[f]	...	15.9 (83) 20.9[g] (~230) 25.3 (10,200) 30.3 (large)	[e]	95–97
$Pd(L^-)_2$	1.516	...	22.1 (320) 29.4 (large)	[e]	115–118
$Co(L^+)_3Cl_6$	1.490	2.450[f] 2.570[f]	15.6 (500) 20.8[g] (~730) 27.4 (17,000) 31.3 (25,000)	623	Loses HCl and decomposes
$Ni(L^+)_2Cl_4$	1.510	2.395[f] 2.575[f]	15.8 (40) 20.3[g] (~70) 23.0[g] (~330) 25.3 (1250) 31.3 (38,000)	436	203–205 dec
$Pd(L^+)_2Cl_4$	1.505	2.440[f] 2.580[f]	22.2 (326) 29.0[g] (~11,000)	467	242 dec
$Co((et)_2dtc)_3$[h]	1.489	...	15.5 (~100) 20.8[g] (~600) 25.4[g] (~9000) 27.8[g] (~12,000) 31.0 (~20,000)	...	...
$Ni((et)_2dtc)_2$[h]	1.518	...	15.8 21.2[g] 23.4[g] 25.8 (~6000) 30.6 (~32,000)	...	...
$Pd((et)_2dtc)_2$[h]	1.521	...	22.2 28.8 (large)	...	...

[a] Spectral data are in kilokaysers (kK). [b] N–H stretching frequency of tertiary amine hydrochloride (see text). [c] ε is the molar extinction coefficient in l. mol^{-1} cm^{-1}. [d] Molar conductance in ohm^{-1} mol^{-1} cm^2 in water. [e] Nonelectrolyte in benzene. [f] Broad. [g] Shoulder. [h] Optical and infrared data taken from ref 7 and 8, respectively; $(et)_2dtc$ is N,N-diethyldithiocarbamate.

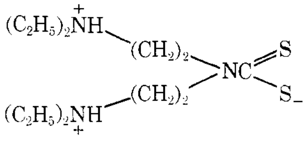
Results and Discussion

Ligands.—It is well known that primary and secondary amines react with carbon disulfide to give dithiocarbamates.[9] If the reaction involves a diamine in which one of the amine groups is tertiary, a zwitterion is produced, since the tertiary nitrogen atom is not capable of reacting with carbon disulfide.[10,11] It follows that reaction of carbon disulfide with triamines with one secondary and two tertiary amine groups will produce a dithiocarbamate which can be forced to carry a net positive charge by protonation of both tertiary nitrogen atoms. In this work such a dithiocarbamate has been prepared from the reaction of carbon disulfide with 1,1,7,7-tetraethyldiethylenetriamine, as shown by

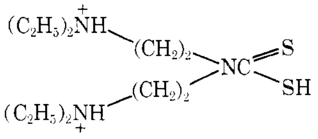


L (1)

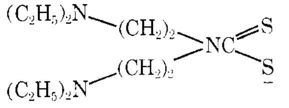
In eq 1 and in the Experimental Section, L is referred to as an acid. However, there is little question that the compound actually exists in the zwitterionic form, since the infrared spectrum of L clearly shows broad bands centered at 2640 and 2700 cm^{-1} which are characteristic of tertiary amine hydrochlorides.[12] L is amphiprotic and may react with 1 or 2 mol of a protonic acid to provide L^+ and L^{2+}, respectively, or with 1 mol of base to give L^-. L^+ was isolated only as a chelate,



L^+



L^{2+}



L^-

while L^{2+} was isolated as a white, water-soluble chloride, but was not characterized beyond infrared spectral measurements. L^- was isolated as described above. The ions L^+ and L^{2+} appear to represent the first reported dithiocarbamates which carry a net positive charge.

Complexes.—In this work two series of complexes have been synthesized. The first series includes $Co(L^-)_3$, $Ni(L^-)_2$, and $Pd(L^-)_2$, in which the ligands carry a charge of −1. Thus, these three complexes are similar to those which have been reported previously.[7,8,13–15] These three stable nonelectrolytes appear to be notable only in that they are soluble in many organic solvents. Most dithiocarbamate complexes, in contrast, are only slightly soluble.[13–15] It should be pointed out that there is no evidence for

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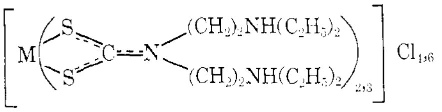
coordination of the tertiary nitrogen atoms. This is not surprising in view of the low tendency of planar dithiocarbamate complexes to form adducts with nitrogenous bases[14] and in view of the poor coordinative properties of monodentate, tertiary amines.[16]

The second series of compounds prepared in this work includes $Co(L^+)_3Cl_6$, $Ni(L^+)_2Cl_4$, and $Pd(L^+)_2Cl_4$, in which the dithiocarbamate ligand carries a *net* positive charge. To our knowledge, there are no other reports of compounds of this type. These three complexes were isolated as anhydrous crystalline solids which are stable in dry air. When exposed to atmospheric moisture the compounds become hydrated, but are not further affected. Thus, the compounds are intermediate in behavior between the phosphorus complexes reported by Meek,[4] which are not affected by water, and the amine complexes reported by Quagliano,[1-3] which are decomposed by water.

The nickel(II) and palladium(II) complexes were prepared in two different ways. The first involved the reaction of Ni^{2+} and Pd^{2+} with the positively charged ligand L^+, which was prepared in solution by treating L with HCl. In the second procedure $Ni(L^-)_2$ and $Pd(L^-)_2$ were protonated in solution with HCl. The cobalt complex was prepared only by protonation of $Co(L^-)_3$.

The success and convenience of the second procedure can be attributed to the great resistance of the metal–sulfur bonds to attack by acids and to the ready availability of the noncoordinated amine groups. The complexes are formulated with the structure



where M = Ni^{2+}, Pd^{2+}, or Co^{3+}, in which the cobalt complex is octahedral and the nickel and palladium complexes are planar.

Structures of the type $[L^+]_{2,3}[MCl_{4,6}]$ are not consistent with the optical spectral data presented in Table I. The molar conductances given in Table I are consistent with the formulation of the Ni(II) and Pd(II) complexes as 4:1 electrolytes, although the conductance values are slightly lower than those normally expected.[17] This may indicate that there is incomplete dissociation in the solutions. The very high molar conductance of the Co(III) complex is also consistent with 6:1 electrolyte behavior. However, there is a paucity of comparable data owing to the rarity of such highly charged cations. Although the hexapositive cation reported here is not unique, it represents a rare example of a monomeric cobalt(III) chelate with a formal charge of +6.

The infrared spectra exhibit two types of bands which are of direct structural significance. First, the broad bands in the 2400–2600-cm^{-1} region are indicative of the quaternary ammonium groups.[12] Second, the bands at *ca.* 1500 cm^{-1} are characteristic of dithiocarbamate complexes in which there is a high contribution from canonical forms involving structures of the type $(S_2^-)C{=}N^+R_2$.[8,14,15] It should be pointed out that the C=N bands are sharp in the electrolytes, whereas the C=N bands usually are broad in nonelectrolyte dithiocarbamate complexes. The position of the band, however, is not appreciably affected by the presence of the positive charges.[8]

It can be concluded from this study that the presence of positive charges on dithiocarbamate ligands has little effect on the coordination properties of the ligands or on the properties of the complexes formed from these ligands, except for an alteration of solubility characteristics.

Acknowledgment.—This work was supported by the National Science Foundation.

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Revised "Cluster" Raman Frequencies for $Pb_6O(OH)_6^{4+}$[1]

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Recently we reported the Raman spectrum of crystals known to have the composition $Pb_3(OH)_4(ClO_4)_2$ and thought to contain $Pb_6(OH)_8^{4+}$ ions.[2] On the basis of what appeared to be three bands below 200 cm^{-1}, with frequency ratios 2:1.32:0.95, it was suggested that the lead atoms were arranged in an octahedron.[3] Similar bands were observed for the hexanuclear hydroxide complex of the isoelectronic Bi(III), $Bi_6(OH)_{12}^{6+}$, in which the bismuth atoms are known to be octahedrally arranged.[4] Furthermore the frequency ratios $\nu_{A_{1g}}/\nu_{T_{2g}}/\nu_{E_g} = 2/\sqrt{2}/1$, predicted[3] for an octahedron of like atoms, neglecting ligands and interaction force constants, are quite close to the observed ratios. It was suggested further that the hydroxide ligands might be located over the eight octahedral faces, giving the complex a structure like that of $Mo_6Cl_8^{4+}$. Indeed a normal-coordinate analysis based on the proposed structure satisfactorily accounted for all of the observed Raman and infrared features.[3]

An X-ray crystal structure determination[5] has now shown the Raman prediction to be incorrect, however.

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[1] This investigation was supported by Public Health Service Grant GM-13498 from the National Institute of General Medical Sciences.

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