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Characterization of Novel Binuclear Ytterbium Compounds

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The reaction of solutions of ytterbium in liquid ammonia with cyclopentadiene has been used to prepare ytterbium cyclopentadienides. The products of the reaction have been reported to be $YbCp_3$ and various other species, among them $YbCp_2NH_2$.[1,2] We have reexamined the reaction and have isolated three products by fractional sublimation of the reaction mixture after removing the ammonia and the cyclopentadiene. The products in question, deep green, yellow, and red compounds, sublime at 150, 170, and 360° respectively, at a pressure of about 10 μ. The first compound has been known for some time to be $YbCp_3$. The third compound, which was previously thought to be $YbCp_2H$,[3] proves to be $YbCp_2$ on the basis of mass spectral analysis and nmr, which shows a resonance due to Cp protons at τ 4.6. This agrees with the value obtained for $YbCp_2$ prepared by other methods.[3] We wish to discuss the structure of the second compound. The compound was identified as a binuclear Yb compound by examination of the complex isotopic pattern of the various molecular ions in the mass spectrum. Similar isotopic patterns have been observed for all ions with $m/e > 371$ ($YbCp_3$). This pattern contained many more lines than the simple, distinctive Yb isotopic pattern and was assigned to a Yb_2 compound. Since the ion of greatest intensity corresponded to $Yb_2Cp_3N_2H_4$, we have calculated its expected intensity pattern, taking into account the isotopic composition of Yb and also using the fact that 15% of the molecules have one ^{13}C in the three cyclopentadienide groups. The comparison of the pattern calculated with that observed appears in Table I.

TABLE I
THEORETICAL AND EXPERIMENTAL ION ABUNDANCES FOR $Yb_2Cp_3N_2H_4$

m/e	Theoret	Exptl	m/e	Theoret	Exptl
568	0.8	0.9	575	15.5	15.6
569	3.1	3.2	576	5.6	6.2
570	6.7	6.4	577	7.6	7.6
571	10.8	10.6	578	1.1	1.4
572	15.6	14.8	579	1.4	1.6
573	17.2	16.6	580	0.2	0.3
574	14.4	14.6			

As one can see, the agreement is good. This agreement allows us to assign isotopic compositions to each peak in the pattern and, since the m/e ratios of the peaks were determined by peak matching, to obtain a formula for the species responsible for the pattern. The complete mass spectrum of the compound helps remove ambiguities in the molecular composition of the species. This spectrum, in which only the $Yb^{173}Yb^{173}$ peaks are shown for each ion, appears in Table II.

TABLE II
MASS SPECTRUM OF COMPOUND II IN THE HIGH MASS REGION USING 70-V ELECTRONS

	m/e	Rel intens		m/e	Rel intens
$Yb_2Cp_4N_2H_4^+$	638	17	$Yb_2Cp_2N_2H_4^+$	508	6
$Yb_2Cp_4NH^+$	621	3	$Yb_2Cp_2NH^+$	491	15
$Yb_2Cp_3N_2H_4^+$	573	100	$Yb_2Cp_2^+$	476	2
$Yb_2Cp_3NH^+$	556	14	$Yb_2CpN_2H_4^+$	443	5
$Yb_2Cp_3^+$	541	4	Yb_2CpNH^+	426	10

The most intense peak centered at m/e 573 proves to be $Yb_2Cp_3N_2H_4$. This assignment is supported by the fact that the next two groups at lower m/e correspond to loss of NH_3 followed by NH, so that the species have the formulas $Yb_2Cp_3N_2H_4$, Yb_2Cp_3NH, and Yb_2Cp_3. Also, peaks are observed at m/e 638 and 621 which correspond to $Yb_2Cp_4N_2H_4$ and Yb_2Cp_4NH. Successive loss of the various cyclopentadiene, NH, and NH_3 moieties is observed at lower m/e. Furthermore, it appears that Yb_2 ions containing less than three cyclopentadiene rings are more stable as NH^+ ions while ions with three or more cyclopentadienes are more stable as $N_2H_4^+$ ions. Currently we have no explanation for this phenomenon.

It is clear that we are dealing with a dimeric species, but it is not obvious whether the parent is $Yb_2Cp_3N_2H_4$ or $Yb_2Cp_4N_2H_4$ or a mixture. Although hampered by the disparity in intensities, evidence for a mixture was obtained by appearance potential measurements, which yield appearance potentials of 8.7 ± 0.2 and 8.4 ± 0.2 eV for $Yb_2Cp_4N_2H_4$ and $Yb_2Cp_3N_2H_4$, respectively. Thus, it is very unlikely that $Yb_2Cp_3N_2H_4$ results from the decomposition of $Yb_2Cp_4N_2H_4$ since the appearance potentials of species such as $YbCp_3^+/YbCp_3$ and $YbCp_2^+/YbCp_3$ or $YbCp_2/YbCp_2$ and $YbCp^+/YbCp_2$ differ by about 2–3 eV.[4] Also, the possibility that $Yb_2Cp_4N_2H_4$ might be due to an ion–molecule reaction in the mass spectrometer source was discounted since the relatively high intensity of the $Yb_2Cp_4N_2H_4$ peaks is not characteristic of an ion–molecule product. Elemental analyses were inconclusive although they tended to support the presence of a mixture.

The most logical proposal is that we have a mixture of $Yb_2Cp_4N_2H_4$, which may have amide bridges like the weak chlorine bridges suggested for $Yb(CH_3Cp)_2Cl$ in benzene solution,[5] and $Yb_2Cp_3N_2H_4$, which seems to have two labile amides and, thus, some type of bridging cyclopentadienes as suggested for the "triple-decker"

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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.

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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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