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Identification of an Extensive Series of Cationic Silver Heterometallic Dithiocarbamate Complexes and Observation of Catalytic Ligand-Exchange Reactions by Electrospray Mass Spectrometry

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The metal-metal-bonded cations $[Ag_2Pt_3(R_2dtc)_6]^{2+}$, consisting of $Pt(R_2dtc)_2$ units acting as ligands toward Ag(I), are observed in electrospray mass spectra as intact ions and also as the monoanion adducts $[Ag_2Pt_3(R_2dtc)_6X]^+$ ($X^- = ClO_4^-, NO_3^-$). When solutions containing two different $Pt(R_2dtc)_2$ complexes and Ag(I) are mixed, there is global scrambling of dithiocarbamate ligands on platinum in the Ag/Pt/R_2dtc cations within 1 h, which is much faster than exchange in the absence of Ag(I). $Hg(R_2dtc)_2$ complexes also act as ligands toward Ag(I), and the cations $[AgHg_2(R_2dtc)_4]^+$ are readily observed. Mixtures of two different $Hg(R_2dtc)_2$ complexes with Ag(I) give the expected global scrambling of the dithiocarbamates on mercury. Interaction between $M(R_2dtc)_3$ (M = Co, Rh, Ir) and Ag(I) leads to the observation of $[AgM_2(R_2dtc)_6]^+$ cations, and mixing of different $M(R_2dtc)_3$ compounds with Ag(I) leads to exchange of complete $M(R_2dtc)_3$ units on Ag but not global dithiocarbamate ligand exchange on cobalt. However, fast global exchange of dithiocarbamate ligands on cobalt and mercury, as well as interchange of metals to give trimetallic species containing Ag, Co, and Hg, is observed when mixtures of $Co(R_2dtc)_3$, $Hg(R'_2dtc)_2$, and Ag(I) are examined by ESMS. Similar global ligand exchange does not occur when $Rh(R_2dtc)_3$ or $Ir(R_2dtc)_3$ is mixed with $Hg(R'_2dtc)_2$ and Ag(I), although exchange of complete metal dithiocarbamate units on Ag(I) does still occur to give mixed Ag/Rh/Hg cations. Sulfur insertion occurs with the iridium complexes to give $[AgIr_2(R_2dtc)_5(R_2dtcS)]^+$ and $AgIr_2(R_2dtc)_4(R_2dtcS)_2]^+$. These results indicate that an extensive new chemistry of neutral metal dithiocarbamates exists in which they behave as ligands toward metal cations. Reaction of silver salts with the dithiocarbamates of Zn(II) and Pb(II) leads to formation of non-silver-containing metal-rich dithiocarbamate cations of the types $[M_2(R_2dtc)_3]^+$ and $[M_2(R_2dtc)_5]^+$ (M = Zn, Pb). Silver(I) salts simply oxidize the dithiocarbamates of Fe(III) and Ni(II) to give the known $[Fe(R_2dtc)_3]^+$ and $[Ni(R_2dtc)_3]^+$ species.

Introduction

Homo- and heterometallic polynuclear chemistry has been an area of intense interest in both organometallic[1] and inorganic chemistry.[2] In organometallic chemistry, Shaw and co-workers[3] have investigated a number of heterometallic systems bridged by polyphosphine and similar ligands. In inorganic chemistry, compounds such as $[Pt(SnCl_3)_5]^{3-}$, held together only by direct metal–metal bonds,[4] have also attracted considerable interest, and mixed-metal clusters such as $[MM'_2(RCOO)_6(H_2O)_3]^+$ (M = Cr, Fe, Mn, etc.) have been widely used to study magnetic interactions between metal centers.[5]

Metal dithiocarbamates (dithiocarbamate = S_2CNR_2 = R_2dtc) have also been the subject of extensive studies for many years, and their chemistry has been reviewed several times.[6] In recent times, a major interest has been the redox properties of dithiocarbamate complexes[7] and the ability of the ligand to stabilize unusually high oxidation states of transition metals, for example Fe(IV), Ni(IV), and Cu(III). Although there are a few examples of dimeric dithiocarbamato cations of the type $[M_2(R_2dtc)_5]^+$ (M = Co,[8] Rh,[9] Ru,[10] Os,[11] etc.), most dithiocarbamate complexes are monomeric in solution although some do crystallize in polymeric forms.[12]

Kawamura and co-workers[13,14] recently reported remarkable reactions between silver perchlorate and platinum(II) dithiocarbamate compounds, $Pt(R_2dtc)_2$. They first examined the reaction of $AgClO_4$ with $Pt(Et_2dtc)_2$ in dichloromethane and demonstrated by spectrophotometric methods that several species are formed in solution, depending upon the stoichiometry. The most stable product was formed at $AgClO_4$:$Pt(Et_2dtc)_2$ = 2:3, and it was formulated as $[Ag_2\{Pt(Et_2dtc)_2\}_3]^{2+}$.[13] A crystal structure determination on the isolated solid revealed a polymeric heterometallic cationic structure of this formula, and its most striking feature was the presence of direct unsupported Ag–Pt bonding, with weak sulfur bridging being present in only some of the metal–metal interactions. Even more remarkable are the corresponding $Pt(i\text{-}Pr_2dtc)_2$ and $Pt(n\text{-}Bu_2dtc)_2$ compounds, for which X-ray crystallography revealed discrete $[Ag_2\{Pt(Et_2dtc)_2\}_3]^{2+}$ cations.[14] There are no sulfur bridging atoms, and the cations are held together only by metal–metal interactions. The five metal atoms can be regarded as forming a trigonal bipyramid, and the undistorted $Pt(R_2dtc)_2$ units are oriented in the equatorial positions with their planar geometries parallel to the Ag–Ag axis. These compounds represent a class of metal complex with neutral

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metal dithiocarbamate ligands whose structures are reminiscent of the $[Pt(SnCl_3)_5]^{3-}$ ion in the sense that they contain only metal–metal bonding.

In a recent study,[15] we examined solutions of cationic mercury- and cadmium-rich dithiocarbamato complexes by electrospray mass spectrometry (ESMS) and found that all species transferred to the gas phase were of the type $\{[M(R_2dtc)]^+ + nM(R_2dtc)_2\}$ (M = Hg, Cd; n = 1–3); that is, they too could be regarded as complexes of a cation with the neutral metal bis(dithiocarbamate) complexes acting as ligands. However, in this case it is believed that the structures are sulfur bridged and do not involve metal–metal bonding. Analogies were made with the solid-state structures of $[M_2(R_2dtc)_5]^+$ compounds (M = Co, Rh, Ru, Os) in which a metal tris(dithiocarbamate) unit can also be regarded as a ligand coordinated to a metal(III) bis(dithiocarbamate) cation through shared sulfur atoms. For a number of these systems, spectroscopic measurements show that the structures are retained in solution, and for $[Co_2(R_2dtc)_5]^+$ and $[Rh_2(R_2dtc)_5]^+$, the cations have been observed by ESMS.[16] It was suggested[15] that the tetrahedral $M(R_2dtc)_2$ units were formally analogous in their coordination behavior to the $[MS_4]^{2-}$ anions, which have an extensive chemistry as ligands.[17]

ESMS is a powerful new method for examining ionic species in solution. The technique was developed mainly by Fenn and co-workers[18] and has been widely applied to the mass spectrometry of large biomolecules.[19] Recent work in our laboratories[15,16,20-22] showed that ESMS may also be applied with advantage to inorganic and organometallic systems. When the first applications of ESMS to inorganic systems were made,[20] the aim was to demonstrate that the technique could observe single compounds in solution. It was then discovered that when solutions containing rapidly exchanging monomeric species (for example mixed phosphine complexes of Hg(II)) are examined by ESMS, individual components of the mixture are revealed, despite low temperatures being required to observe the components by NMR methods.[21] The application of ESMS to homometallic polynuclear compounds is even more recent. The first examples were the $[Cr_3O(RCOO)_6(H_2O)_3]^+$ cations,[22] which have a relatively inert core, with the highly labile mercury- and cadmium-rich dithiocarbamate cations, some of which were heterometallic, being subsequently investigated.[15] In almost every case, the species known to be present in solution were observed as their intact ions in the ES mass spectra. As more systems are investigated, confidence will continue to increase that ES mass spectra truly reflect the species present in solution.

In this paper, we use the well-characterized $AgClO_4/Pt(R_2dtc)_2$ system to demonstrate that ESMS can readily identify the species in solutions of complex heterometallic dithiocarbamate cationic complexes. We then use the technique to explore the chemistry of other heterometallic silver dithiocarbamate cations and show that previously unknown catalytic dithiocarbamate-exchange reactions commonly occur in these systems.

Experimental Section

$Pt(R_2dtc)_2$,[23] $Hg(R_2dtc)_2$,[24] $Co(R_2dtc)_3$,[8b] $Rh(R_2dtc)_3$,[25] and $Ir(R_2dtc)_3$[26] were prepared as described previously. Solutions of the compounds (2.0 mM in dichloromethane) were mixed with various proportions (usually 3:2 or 2:1) of silver salts dissolved in acetonitrile. This solution was then diluted 1:10 with methanol.

Electrospray mass spectra were obtained with a VG Bio-Q triple-quadrupole mass spectrometer[27] using a water/methanol/acetic acid (50:50:1%) mobile phase. The diluted solutions of the compounds, prepared as described above, were injected directly into the spectrometer via a Rheodyne injector equipped with a 10-μL loop. A Phoenix 20 micro LC syringe pump delivered the solution to the vaporization nozzle of the electrospray ion source at a flow rate of 3 μL min^{-1}. Nitrogen was used as the drying gas and for nebulization, with flow rates of approximately 3 L min^{-1} and 100 mL min^{-1}, respectively. Pressure in the mass analyzer region was usually about 3×10^{-5} Torr. The compounds in this study gave strong signals in their ES mass spectra, and typically four to eight signal-averaged spectra were required to give a good signal-to-noise ratio. Increasing the voltage on the first skimmer electrode (B1) may be used to induce collisionally activated decomposition in the high-pressure region of the ion source. In this study, measurements were made at B1 = 40 V unless stated otherwise.

Results and Discussion

All peaks in the electrospray mass spectra are identified by the m/z value of the most abundant peak in the isotopic mass distribution. In all cases, the agreement between experimental and calculated isotopic mass distributions was excellent.

$Pt(R_2dtc)_2/Ag(I)$ Systems. The ES mass spectrum of a solution containing $Pt(n\text{-}Bu_2dtc)_2$ and $AgClO_4$ (3:2) contains a number of strong peaks assignable to mixed platinum–silver complexes, and data are summarized in Table 1. The intact cation $[Ag_2Pt_3(Bu_2dtc)_6]^{2+}$, known to be present in the solids isolated from such solutions, is observed at m/z 1013, and the isotope pattern confirms this peak is due to a doubly charged cation. Another peak at m/z 2126 is assigned to the perchlorate adduct $[Ag_2Pt_3(Bu_2dtc)_6(ClO_4)]^+$. Quite frequently, doubly charged cations are observed in ESMS as their monoanion adducts, but it is interesting that in this case the cation prefers perchlorate to the acetate which is present in the mobile phase. A small peak at m/z 808 is due to $[Pt(Bu_2dtc)_3]^+$, and other peaks at m/z 1315 and 1919 are assigned to $[AgPt_2(Bu_2dtc)_4]^+$ and $[AgPt_3(Bu_2dtc)_6]^+$, respectively, which may be regarded as fragments of $[Ag_2Pt_3(Bu_2dtc)_6]^{2+}$. The reaction between $Pt(Bu_2dtc)_2$ and $AgNO_3$ gives an identical ES mass spectrum except that $[Ag_2Pt_3(Bu_2dtc)_6(NO_3)]^+$ (m/z 2088) is observed instead of $[Ag_2Pt_3(Bu_2dtc)_6(ClO_4)]^+$. The ES mass spectrum of a solution containing $Pt(i\text{-}Pr_2dtc)_2$ and $AgClO_4$ gives corresponding peaks, and data are summarized in Table 1. Thus ESMS can detect the polynuclear heterometallic dithiocarbamate cationic species known to be present in these solutions.

The ES mass spectrum of a solution containing $Pt(Et_2dtc)_2$ and $AgNO_3$ (3:2) is also similar. Figure 1a shows the spectrum at a B1 voltage of 40 V, and the peaks (m/z) are assigned to $[Pt(Et_2dtc)_3]^+$ (640), the intact ion $[Ag_2Pt_3(Et_2dtc)_6]^{2+}$ (845), $[AgPt_2(Et_2dtc)_4]^+$ (1091), $[AgPt_3(Et_2dtc)_6]^+$ (1582), and the

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Table 1. ESMS Data for Solutions Containing $Pt(R_2dtc)_2$ and Silver Salts

mixture	ions (*m/z*)
$Pt(Pr_2dtc)_2 + AgClO_4$	$[Pt(Pr_2dtc)_3]^+$ (724); $[Ag_2Pt_3(Pr_2dtc)_6]^{2+}$ (929); $[AgPt_2(Pr_2dtc)_4]^+$ (1203); $[AgPt_3(Pr_2dtc)_6]^+$ (1750); $[Ag_2Pt_3(Pr_2dtc)_6(ClO_4)]^+$ (1958)
$Pt(Bu_2dtc)_2 + AgClO_4$	$[Pt(Bu_2dtc)_3]^+$ (808); $[Ag_2Pt_3(Bu_2dtc)_6]^{2+}$ (1013); $[AgPt_2(Bu_2dtc)_4]^+$ (1315); $[AgPt_3(Bu_2dtc)_6]^+$ (1919); $[Ag_2Pt_3(Bu_2dtc)_6(ClO_4)]^+$ (2126)
$Pt(Et_2dtc)_2 + AgNO_3$	$[Pt(Et_2dtc)_3]^+$ (640); $[Ag_2Pt_3(Et_2dtc)_6]^{2+}$ (845); $[AgPt_2(Et_2dtc)_4]^+$ (1091); $[AgPt_3(Et_2dtc)_6]^+$ (1582); $[Ag_2Pt_3(Et_2dtc)_6(NO_3)]^+$ (1752)
$Pt(Et_2dtc)_2 + Pt(Bu_2dtc)_2 + AgNO_3$ (B1 = 50 V)	$[Ag_2Pt_3(Et_2dtc)_6]^{2+}$ (845); $[Ag_2Pt_3(Et_2dtc)_5(Bu_2dtc)]^{2+}$ (873); $[Ag_2Pt_3(Et_2dtc)_4(Bu_2dtc)_2]^{2+}$ (901); $[Ag_2Pt_3(Et_2dtc)_3(Bu_2dtc)_3]^{2+}$ (929); $[Ag_2Pt_3(Et_2dtc)_2(Bu_2dtc)_4]^{2+}$ (957); $[Ag_2Pt_3(Et_2dtc)(Bu_2dtc)_5]^{2+}$ (985); $[Ag_2Pt_3(Bu_2dtc)_6]^{2+}$ (1013); $[AgPt_2(Et_2dtc)_4]^+$ (1091); $[AgPt_2(Et_2dtc)_3(Bu_2dtc)]^+$ (1147); $[AgPt_2(Et_2dtc)_2(Bu_2dtc)_2]^+$ (1203); $[AgPt_2(Et_2dtc)(Bu_2dtc)_3]^+$ (1259); $[AgPt_2(Bu_2dtc)_4]^+$ (1315); $[Ag_2Pt_2(Et_2dtc)_2(Bu_2dtc)_2(NO_3)]^+$ (1372); $[Ag_2Pt_2(Et_2dtc)(Bu_2dtc)_3(NO_3)]^+$ (1428); $[Ag_2Pt_2(Bu_2dtc)_4(NO_3)]^+$ (1485); $[Ag_2Pt_3(Et_2dtc)_6(NO_3)]^+$ (1752); $[Ag_2Pt_3(Et_2dtc)_5(Bu_2dtc)(NO_3)]^+$ (1808); $[Ag_2Pt_3(Et_2dtc)_4(Bu_2dtc)_2(NO_3)]^+$ (1864); $[Ag_2Pt_3(Et_2dtc)_3(Bu_2dtc)_3(NO_3)]^+$ (1920); $[Ag_2Pt_3(Et_2dtc)_2(Bu_2dtc)_4(NO_3)]^+$ (1976); $[Ag_2Pt_3(Et_2dtc)(Bu_2dtc)_5(NO_3)]^+$ (2032); $[Ag_2Pt_3(Bu_2dtc)_6(NO_3)]^+$ (2088)
$Pt(Pr_2dtc)_2 + Pt(Bu_2dtc)_2 + AgClO_4$	$[Ag_2Pt_3(Pr_2dtc)_6]^{2+}$ (929); $[Ag_2Pt_3(Pr_2dtc)_5(Bu_2dtc)]^{2+}$ (943); $[Ag_2Pt_3(Pr_2dtc)_4(Bu_2dtc)_2]^{2+}$ (957); $[Ag_2Pt_3(Pr_2dtc)_3(Bu_2dtc)_3]^{2+}$ (971); $[Ag_2Pt_3(Pr_2dtc)_2(Bu_2dtc)_4]^{2+}$ (985); $[Ag_2Pt_3(Pr_2dtc)(Bu_2dtc)_5]^{2+}$ (999); $[Ag_2Pt_3(Bu_2dtc)_6]^{2+}$ (1013); $[AgPt_2(Pr_2dtc)_4]^+$ (1203); $[AgPt_2(Pr_2dtc)_3(Bu_2dtc)]^+$ (1231); $[AgPt_2(Pr_2dtc)_2(Bu_2dtc)_2]^+$ (1259); $[AgPt_2(Pr_2dtc)(Bu_2dtc)_3]^+$ (1287); $[AgPt_2(Bu_2dtc)_4]^+$ (1315); $[AgPt_3(Pr_2dtc)_6]^+$ (1750); $[AgPt_3(Pr_2dtc)_5(Bu_2dtc)]^+$ (1778); $[AgPt_3(Pr_2dtc)_4(Bu_2dtc)_2]^+$ (1806); $[AgPt_3(Pr_2dtc)_3(Bu_2dtc)_3]^+$ (1834); $[AgPt_3(Pr_2dtc)_2(Bu_2dtc)_4]^+$ (1862); $[AgPt_3(Pr_2dtc)(Bu_2dtc)_5]^+$ (1891); $[AgPt_3(Bu_2dtc)_6]^+$ (1919); $[Ag_2Pt_3(Pr_2dtc)_6(ClO_4)]^+$ (1958); $[Ag_2Pt_3(Pr_2dtc)_5(Bu_2dtc)(ClO_4)]^+$ (1986); $[Ag_2Pt_3(Pr_2dtc)_4(Bu_2dtc)_2(ClO_4)]^+$ (2014); $[Ag_2Pt_3(Pr_2dtc)_3(Bu_2dtc)_3(ClO_4)]^+$ (2042); $[Ag_2Pt_3(Pr_2dtc)_2(Bu_2dtc)_4(ClO_4)]^+$ (2070); $[Ag_2Pt_3(Pr_2dtc)(Bu_2dtc)_5(ClO_4)]^+$ (2098); $[Ag_2Pt_3(Bu_2dtc)_6(ClO_4)]^+$ (2126)

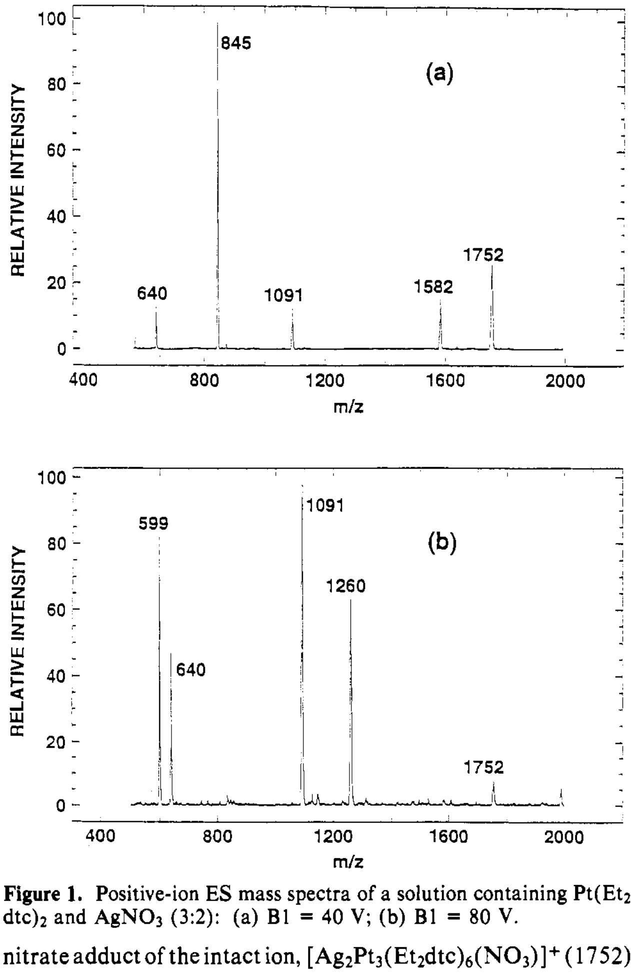

Figure 1. Positive-ion ES mass spectra of a solution containing $Pt(Et_2dtc)_2$ and $AgNO_3$ (3:2): (a) B1 = 40 V; (b) B1 = 80 V.

nitrate adduct of the intact ion, $[Ag_2Pt_3(Et_2dtc)_6(NO_3)]^+$ (1752). As the B1 skimmer voltage is increased to 80 V, the relative intensities of the peaks due to the intact ion and its nitrate adduct decrease, that of the peak at *m/z* 1091 increases, and new peaks appear (Figure 1b). The peaks at *m/z* 599 and 1260 are assigned to $[AgPt(Et_2dtc)_2]^+$ and $[Ag_2Pt_2(Et_2dtc)_4(NO_3)]^+$, respectively, which, together with $[AgPt_2(Et_2dtc)_4]^+$, are logical product ions from collisionally activated decompositions of the intact ion, or its nitrate adduct, following loss of silver atoms or complete $Pt(Et_2dtc)_2$ ligands.

The original work[13,14] on these systems reported very similar solution spectral behaviors for the diethyl-, dipropyl-, and dibutyldithiocarbamate derivatives, and it was only in the solid state that the diethyldithiocarbamate differed from the others. The ES mass spectra imply that all the platinum dithiocarbamates form the same type of complex in solution with Ag(I) and the differences in the crystal structures are merely the result of packing factors in the solid state.

In an attempt to prepare cationic silver species with mixed $Pt(R_2dtc)_2$ ligands to demonstrate lability in the Ag–Pt bonds, solutions containing $Pt(Et_2dtc)_2/AgClO_4$ (3:2) and $Pt(Bu_2dtc)_2/AgClO_4$ (3:2) were mixed. The ES mass spectra of a diluted sample, recorded with a B1 voltage of 50 V, are much more complicated than anticipated and show that, instead of merely the expected simple exchange of $Pt(R_2dtc)_2$ units, there is global scrambling of the $[R_2dtc]^-$ ligands on platinum, giving all possible combinations of $[R_2dtc]^-$ groups in all of the platinum/silver cations. Figure 2a shows the ES mass spectrum of the mixture several minutes after mixing. The strong peaks at *m/z* 845, 901, 957, and 1013 are due to the intact ions $[Ag_2Pt_3(Et_2dtc)_6]^{2+}$, $[Ag_2Pt_3(Et_2dtc)_4(Bu_2dtc)_2]^{2+}$, $[Ag_2Pt_3(Et_2dtc)_2(Bu_2dtc)_4]^{2+}$, and $[Ag_2Pt_3(Bu_2dtc)_6]^{2+}$, respectively, showing that exchange of the $Pt(R_2dtc)_2$ units is indeed quite rapid. The weak peaks between those cited above are evidence that some scrambling of the dithiocarbamate groups has already occurred. A similar pattern is also clearly discernible for the peaks between *m/z* 1752 and *m/z* 2088, which are assigned to the mixed $[Ag_2Pt_3(R_2dtc)_6(NO_3)]^+$ cations. Figure 2b shows the ES mass spectrum for another freshly diluted sample taken about 1 h after the original mixing. It can be seen that the global scrambling of the dithiocarbamate groups on platinum is now essentially complete. The remaining peaks in Figure 2b are assigned to $[AgPt_2(Et_2dtc)_x(Bu_2dtc)_{4-x}]^+$ and $[Ag_2Pt_2(Et_2dtc)_x(Bu_2dtc)_{4-x}(NO_3)]^+$ cations which are identified in Table 1. Parts c and d of Figure 2 show in more detail the *m/z* regions associated with the intact

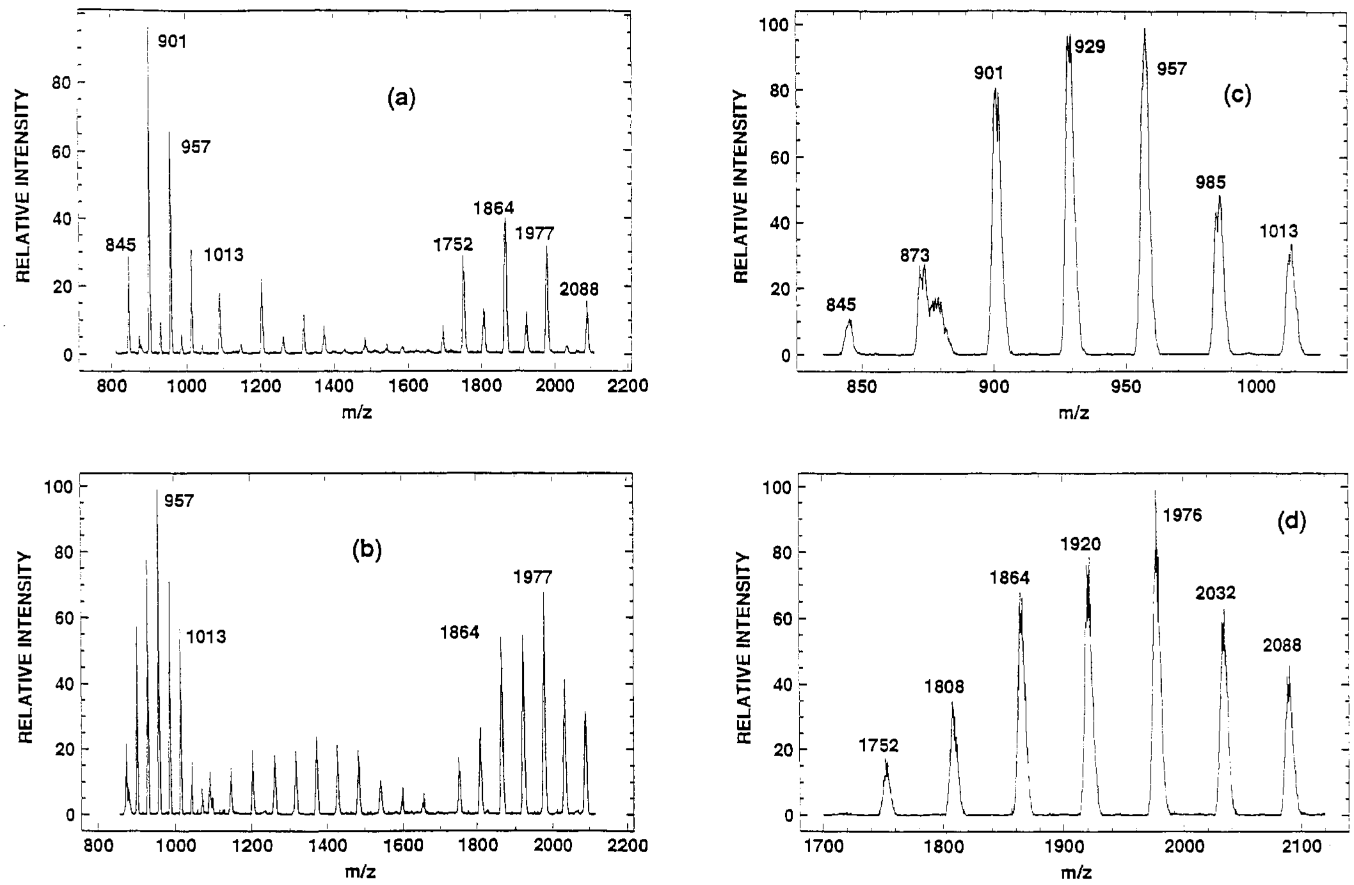

Figure 2. Positive-ion ES mass spectra of a solution containing $Pt(Et_2dtc)_2$, $Pt(Bu_2dtc)_2$, and $AgNO_3$ (3:3:4) at B1 = 50 V: (a) spectrum about 5 min after mixing; (b) spectrum about 1 h after mixing, (c) detail of the *m*/*z* range 800–1100; (d) detail of the *m*/*z* range 1700–2200.

Table 2. ESMS Data for Solutions Containing $Hg(R_2dtc)_2$ and Silver Salts

mixture	ions (*m*/*z*)
$Hg(Et_2dtc)_2 + AgNO_3$	$[Hg_2(Et_2dtc)_3]^+$ (846); $[AgHg_2(Et_2dtc)_4]^+$ (1103)
$Hg(Bu_2dtc)_2 + AgNO_3$	$[Hg_2(Bu_2dtc)_3]^+$ (1014); $[AgHg_2(Bu_2dtc)_4]^+$ (1327)
$Hg(Et_2dtc)_2 + Hg(Bu_2dtc)_2 + AgNO_3$	$[AgHg_2(Et_2dtc)_4]^+$ (1103); $[AgHg_2(Et_2dtc)_3(Bu_2dtc)]^+$ (1159); $[AgHg_2(Et_2dtc)_2(Bu_2dtc)_2]^+$ (1215); $[AgHg_2(Et_2dtc)(Bu_2dtc)_3]^+$ (1271); $[AgHg_2(Bu_2dtc)_4]^+$ (1327)

ions $[Ag_2Pt_3(Et_2dtc)_x(Bu_2dtc)_{6-x}]^{2+}$ (*m*/*z* 845-1013) and their nitrate adducts $[Ag_2Pt_3(Et_2dtc)_x(Bu_2dtc)_{6-x}(NO_3)]^+$ (*m*/*z* 1752-2088).

We have previously shown[28] by platinum-195 NMR spectroscopy that ligand exchange between different $Pt(R_2dtc)_2$ compounds is slow at room temperature, taking a few days to reach equilibrium. In the present system, complete exchange is achieved in less than 1 h, so silver must be catalyzing the reaction, although the mechanism is unknown.

Similar exchange reactions were observed on mixing solutions containing $Pt(Pr_2dtc)_2$ and $Pt(Bu_2dtc)_2$ with added $AgClO_4$. These ES mass spectra were acquired with a B1 voltage of 40 V and soon after mixing showed complete scrambling of $Pt(R_2dtc)_2$ units. After about 1 h, there was also complete scrambling of the dithiocarbamate ligands on platinum, exactly as observed for the $Pt(Et_2dtc)_2/Pt(Bu_2dtc)_2/AgNO_3$ system. Data are summarized in Table 1, and the different species observed in this case are a result of the differing B1 voltages, as described above.

ESMS does not give direct structural information, and it must be conceded that the technique could not have given any indication of the extraordinary structures of the $Ag/Pt(R_2dtc)_2$ cations. X-ray crystallography was indispensable in this system to establish the structure of the cations in the solid phase, but the results prevented above show the ability of the ESMS method to provide detailed additional information on the individual components of complex mixtures in solution from which those solids were crystallized.

$Hg(R_2dtc)_2/Ag(I)$ Systems. In order to establish a direct connection between our previous work[15] demonstrating the coordination of $Hg(R_2dtc)_2$ units as ligands to the $[Hg(R_2dtc)]^+$ cation and the work of Kawamura and co-workers[13,14] on the $Pt(R_2dtc)_2/AgClO_4$ systems, we have used ESMS to examine the reactions between $Hg(R_2dtc)_2$ compounds and Ag(I). Figure 3a shows the ES mass spectrum of a solution containing $Hg(Et_2dtc)_2$ and $AgNO_3$ (2:1). The base peak at *m*/*z* 1103 is assigned to the intact ion $[AgHg_2(Et_2dtc)_4]^+$ (i.e. $[Ag\{Hg(Et_2dtc)_2\}_2]^+$), and the weaker peak at *m*/*z* 846 is due to $[Hg_2(Et_2dtc)_3]^+$ (i.e. $[Hg(Et_2dtc)_2]^+ + Hg(Et_2dtc)_2$, which has been characterized previously.[15] Importantly, there are no ions observed at higher *m*/*z* values and none containing two silver atoms. An exactly analogous ES mass spectrum is observed for a solution of $Hg(Bu_2dtc)_2$ and $AgNO_3$, and data are summarized in Table 2. We believe that in these compounds the $Hg(R_2dtc)_2$ groups are coordinated to the silver atom via sulfur bridges, not by any direct Ag–Hg interaction, and that they are effectively simple $[AgL_2]^+$ cations. This presumption is based upon the crystal structures of the homometallic mercury-rich cations,[24,29] which do not show any metal–metal bonding, and on similarities

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(28) Colton, R.; Tedesco, V. *Inorg. Chem.* **1991**, *30*, 2451.

(29) Bond, A. M.; Hollenkamp, A. F.; Colton, R.; Hoskins, B. F.; McGregor, K.; Tiekink, E. R. T. *Inorg. Chem.* **1991**, *30*, 192.

Table 3. ESMS Data for Solutions Containing $M(R_2dtc)_3$ (M = Co, Rh, Ir) and Silver Salts

mixture	ions (*m/z*)
$Co(Et_2dtc)_3 + AgNO_3$	$[AgCo_2(Et_2dtc)_6]^+$ (1115)
$Co(Pr_2dtc)_3 + AgClO_4$	$[AgCo_2(Pr_2dtc)_6]^+$ (1283)
$Co(Bu_2dtc)_3 + AgNO_3$	$[AgCo_2(Bu_2dtc)_6]^+$ (1451)
$Co(EtBudtc)_3 + AgNO_3$	$[AgCo_2(EtBudtc)_6]^+$ (1283)
$Co(cHxPrdtc)_3 + AgClO_4$	$[AgCo_2(cHxPrdtc)_6]^+$ (1523)
$Co(Oct_2dtc)_3 + AgNO_3$	$[AgCo_2(Oct_2dtc)_6]^+$ (2123)
$Co(EtBudtc)_3 + Co(Oct_2dtc)_3 + AgNO_3$	$[AgCo_2(EtBudtc)_6]^+$ (1283); $[AgCo_2(EtBudtc)_3(Oct_2dtc)_3]^+$ (1703); $[AgCo_2(Oct_2dtc)_6]^+$ (2123)
$Rh(Et_2dtc)_3 + AgNO_3$	$[AgRh_2(Et_2dtc)_6]^+$ (1203); $[Ag_2Rh_2(Et_2dtc)_6(NO_3)]^+$ (1372)
$Rh(cHx_2dtc)_3 + AgNO_3$	$[AgRh_2(cHx_2dtc)_6]^+$ (1851)
$Ir(Et_2dtc)_3 + AgNO_3$	$[AgIr_2(Et_2dtc)_6]^+$ (1381); $[Ag_2Ir_2(Et_2dtc)_6(NO_3)]^+$ (1552)
$Ir(Pr_2dtc)_3 + AgNO_3$	$[AgIr_2(Pr_2dtc)_6]^+$ (1549)

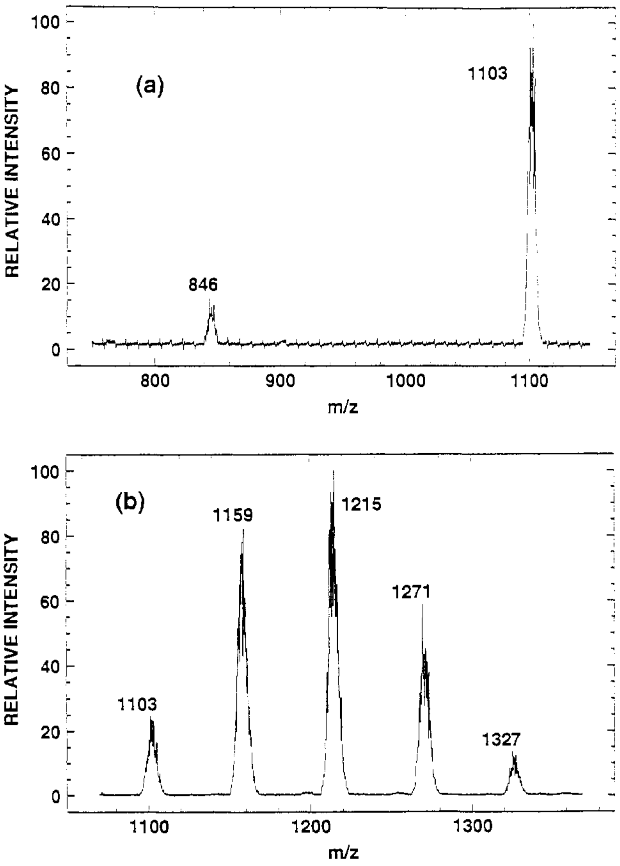

Figure 3. Positive-ion ES mass spectra (B1 = 40 V) of solutions containing (a) $Hg(Et_2dtc)_2$ and $AgNO_3$ (2:1) and (b) $Hg(Et_2dtc)_2$, $Hg(Bu_2dtc)_2$, and $AgNO_3$ (2:2:2).

with the corresponding heterometallic $[Ag\{Co(R_2dtc)_3\}_2]^+$ species, described below, for which metal–metal bonding is inconceivable.

Figure 3b shows the ES mass spectrum for a solution containing $Hg(Et_2dtc)_2$, $Hg(Bu_2dtc)_2$, and $AgNO_3$ (2:2:2). The five peaks are assigned to the mixed heterometallic dithiocarbamate complexes $[AgHg_2(Et_2dtc)_x(Bu_2dtc)_{4-x}]^+$ as detailed in Table 2. It has been previously demonstrated by both mercury-199 NMR measurements[30] and ESMS[15] that dithiocarbamate ligands are labile on mercury, so in this case global scrambling of the dithiocarbamate ligands on mercury to give the statistical distribution was expected.

$M(R_2dtc)_3/Ag(I)$ Systems (M = Co, Rh, Ir). The structures in the solid state of the unsymmetrical form of the dimeric complexes of the type $[M_2(R_2dtc)_5]^+$ (M = Co, Rh, Ru, Os, etc.) can be regarded as consisting of a neutral $M(R_2dtc)_3$ ligand coordinated to a $[M(R_2dtc)_2]^+$ cation via shared sulfur atoms. It seemed to us that a logical extension of the concept that $M(R_2dtc)_3$ groups can act as ligands was to investigate their reactions in solution with Ag(I).

The ES mass spectrum at low collision energy (B1 = 40 V) of a solution of $Co(Et_2dtc)_3$ and $AgNO_3$ (2:1) shows only one peak at *m/z* 1115, which is assigned to $[Ag\{Co(Et_2dtc)_3\}_2]^+$ ($[AgCo_2(Et_2dtc)_6]^+$), and this is confirmed by the isotopic mass distribution pattern. Other cobalt tris(dithiocarbamates) give the corresponding Ag(I) cations, as do the tris(dithiocarbamates) of rhodium(III) and iridium(III), as detailed in Table 3. The ES mass spectrum of a mixture of $Co(EtBudtc)_3$, $Co(Oct_2dtc)_3$, and $AgNO_3$ gave three peaks at *m/z* 1283, 1703, and 2123, assigned to $[AgCo_2(EtBudtc)_6]^+$, $[AgCo_2(EtBudtc)_3(Oct_2dtc)_3]^+$, and $[AgCo_2(Oct_2dtc)_6]^+$. That is, there is exchange of $Co(R_2dtc)_3$ units but no global scrambling of the dithiocarbamate ligands among the cobalt atoms. This type of exchange has been observed previously between $[Co_2(R_2dtc)_5]^+$ cations using both cobalt-59 NMR[8c] and ESMS techniques,[16] but the contrast with the behavior of the silver/platinum systems, in which silver labilizes the relatively inert platinum complexes, is noteworthy.

$M(R_2dtc)_3/Hg(R_2dtc)_2/Ag(I)$ Systems. Since silver readily forms $[AgL_2]^+$ complexes when L is either a tetrahedral $M(R_2dtc)_2$ unit or an octahedral $M(R_2dtc)_3$ unit, a solution of $Co(Oct_2dtc)_3$, $Hg(Bu_2dtc)_2$, and $AgNO_3$ (2:2:2) was prepared and its ES mass spectrum examined in an attempt to observe the unsymmetrical mixed-ligand complex $[Ag\{Co(Oct_2dtc)_3\}\{Hg(Bu_2dtc)_2\}]^+$. The ES mass spectra are much more complicated than expected and show that complete global exchange of the dithiocarbamates between cobalt and mercury has occurred on the time scale of a few minutes. Figure 4a shows the ES mass spectrum of a solution containing $AgNO_3$ and an excess of $Hg(Bu_2dtc)_2$ over $Co(Oct_2dtc)_3$. All of the peaks are identified in Table 4, but the intense ones at *m/z* 1327, 1439, 1500, 1612, and 1724, assigned to $[AgHg_2(Bu_2dtc)_4]^+$, $[AgHg_2(Bu_2dtc)_3(Oct_2dtc)]^+$, $[AgCoHg(Bu_2dtc)_4(Oct_2dtc)]^+$, $[AgCoHg(Bu_2dtc)_3(Oct_2dtc)_2]^+$, and $[AgCoHg(Bu_2dtc)_2(Oct_2dtc)_3]^+$, respectively, are sufficient to show that exchange of the dithiocarbamate ligands on mercury and cobalt has occurred. Figure 4b is an expansion showing the major peaks in more detail. More $Co(Oct_2dtc)_3$ was then added to the original solution and a new dilution made for ESMS. Figure 4c shows that the equilibria in solution have now shifted to favor species containing two cobalt atoms and $[Oct_2dtc]^-$ ligands, and details of the major peaks are shown in Figure 4d. Peaks at *m/z* 1675, 1787, 1836, and 2011 are due to $[AgCo_2(Bu_2dtc)_4(Oct_2dtc)_2]^+$, $[AgCo_2(Bu_2dtc)_3(Oct_2dtc)_3]^+$, $[AgCoHg(Bu_2dtc)(Oct_2dtc)_4]^+$, and $[AgCo_2(Bu_2dtc)(Oct_2dtc)_5]^+$, respectively. The time scale involved between mixing and acquiring data is about 3 min, so the mixture of Ag(I) and $Hg(R_2dtc)_2$ has converted the usually kinetically inert octahedral Co(III) complexes into a very labile system. Similar complete dithiocarbamate ligand exchange occurs between $Co(Oct_2dtc)_3$ and $Hg(Et_2dtc)_2$ upon reaction with Ag(I), and all data are summarized in Table 4. In these cases, there is some overlap of peaks due to the similar mass of Et_2dtc + Co and that of Hg, so not all species are identified individually.

In an attempt to investigate whether the effect of mercury on the system is catalytic, a very small amount of $Hg(Et_2dtc)_2$ was added to the mixture of $Co(Oct_2dtc)_3$, $Co(EtBudtc)_3$, and $AgNO_3$, whose ES mass spectrum has been described earlier. No additional peaks were observed in the mass spectrum, so it appears

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[30] Bond, A. M.; Colton, R.; Dakternieks, D.; Dillon, M. L.; Hauenstein, J.; Moir, J. E. *Aust. J. Chem.* **1981**, *34*, 1393.

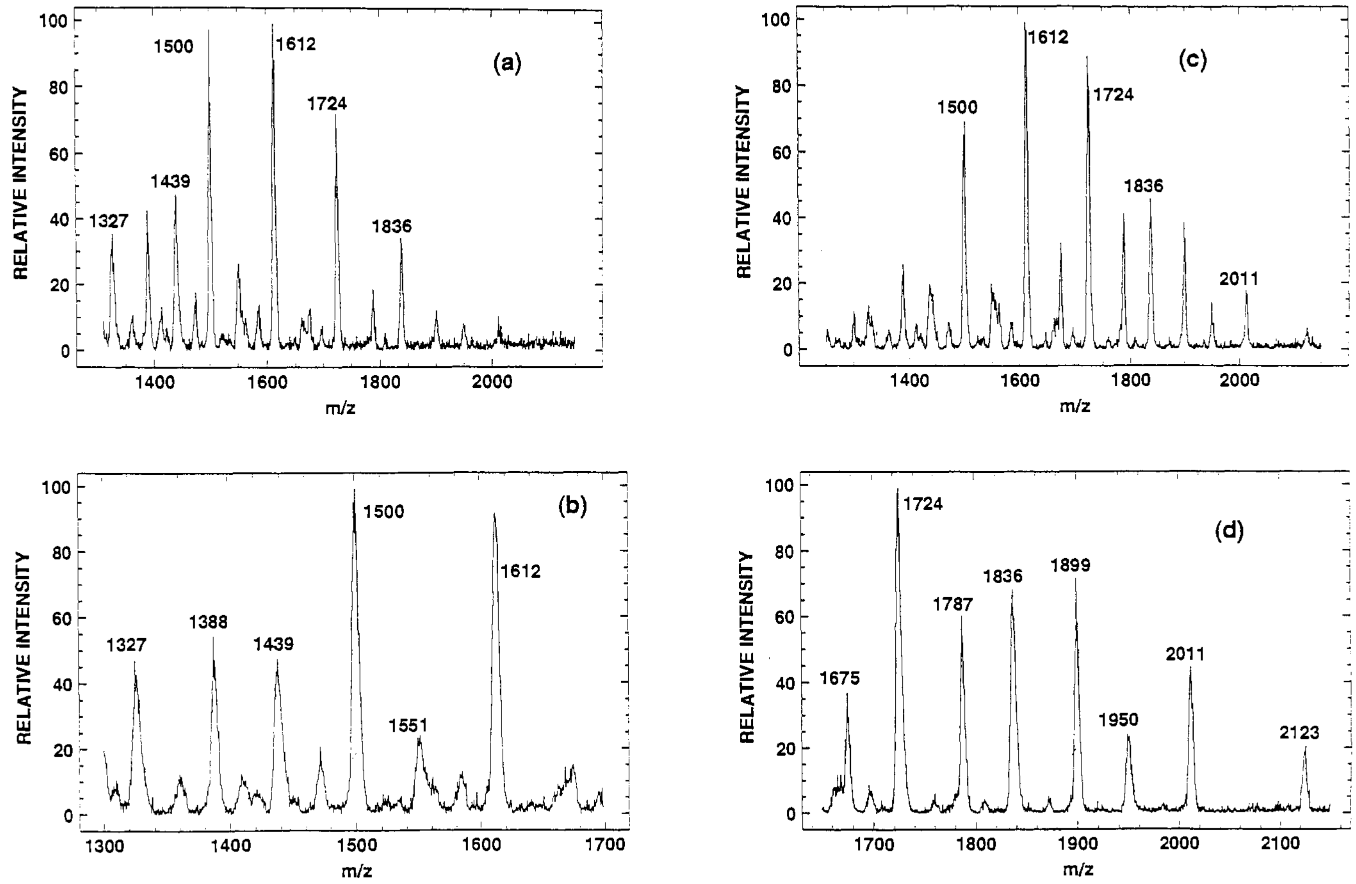

Figure 4. Positive-ion ES mass spectra (B1 = 40 V) of solutions containing $Hg(Bu_2dtc)_2$, $Co(Oct_2dtc)_3$, and $AgNO_3$: (a) spectrum for more $Hg(Bu_2dtc)_2$ than $Co(Oct_2dtc)_3$; (b) detail of the *m/z* range 1300–1800; (c) spectrum for more $Co(Oct_2dtc)_3$ added; (d) detail of the *m/z* range 1500–2200.

Table 4. ESMS Data for Solutions Containing $M(R_2dtc)_3$, $Hg(R_2dtc)_2$, and Silver Salts

mixture	ions (*m/z*)
$Co(Oct_2dtc)_3 + Hg(Bu_2dtc)_2 + AgNO_3$	$[AgHg_2(Bu_2dtc)_4]^+$ (1327); $[AgHg_2(Bu_2dtc)_3(Oct_2dtc)]^+$ (1439); $[AgHg_2(Bu_2dtc)_2(Oct_2dtc)_2]^+$ (1551); $[AgHg_2(Bu_2dtc)(Oct_2dtc)_3]^+$ (1663); $[AgCoHg(Bu_2dtc)_5]^+$ (1388); $[AgCoHg(Bu_2dtc)_4(Oct_2dtc)]^+$ (1500); $[AgCoHg(Bu_2dtc)_3(Oct_2dtc)_2]^+$ (1612); $[AgCoHg(Bu_2dtc)_2(Oct_2dtc)_3]^+$ (1724); $[AgCoHg(Bu_2dtc)(Oct_2dtc)_4]^+$ (1836); $[AgCoHg(Oct_2dtc)_5]^+$ (1950); $[AgCo_2(Bu_2dtc)_6]^+$ (1451); $[AgCo_2(Bu_2dtc)_5(Oct_2dtc)]^+$ (1563); $[AgCo_2(Bu_2dtc)_4(Oct_2dtc)_2]^+$ (1675); $[AgCo_2(Bu_2dtc)_3(Oct_2dtc)_3]^+$ (1787); $[AgCo_2(Bu_2dtc)_2(Oct_2dtc)_4]^+$ (1899); $[AgCo_2(Bu_2dtc)(Oct_2dtc)_5]^+$ (2011); $[AgCo_2(Oct_2dtc)_6]^+$ (2123)
$Co(Oct_2dtc)_3 + Hg(Et_2dtc)_2 + AgNO_3$	$[AgHg_2(Et_2dtc)_2(Oct_2dtc)_2]^+$ (1439); $[AgHg_2(Et_2dtc)(Oct_2dtc)_3]^+$ (1607); $[AgCoHg(Et_2dtc)_5]^+$ (1108); $[AgCoHg(Et_2dtc)_4(Oct_2dtc)]^+$ (1276); $[AgCoHg(Et_2dtc)_3(Oct_2dtc)_2]^+$ (1444); $[AgCoHg(Et_2dtc)_2(Oct_2dtc)_3]^+$ (1612); $[AgCoHg(Et_2dtc)(Oct_2dtc)_4]^+$ (1780); $[AgCo_2(Et_2dtc)_5(Oct_2dtc)]^+$ (1283); $[AgCo_2(Et_2dtc)_4(Oct_2dtc)_2]^+$ (1451); $[AgCo_2(Et_2dtc)_3(Oct_2dtc)_3]^+$ (1619); $[AgCo_2(Et_2dtc)_2(Oct_2dtc)_4]^+$ (1787); $[AgCo_2(Et_2dtc)(Oct_2dtc)_5]^+$ (1955); $[AgCo_2(Oct_2dtc)_6]^+$ (2123)
$Rh(Et_2dtc)_3 + Hg(Bu_2dtc)_2 + AgNO_3$	$[AgRh_2(Et_2dtc)_6]^+$ (1203); $[AgRhHg(Et_2dtc)_3(Bu_2dtc)_2]^+$ (1264); $[AgHg_2(Bu_2dtc)_4]^+$ (1327)
$Ir(Pr_2dtc)_3 + Hg(Et_2dtc)_2 + AgNO_3$	$[AgHg_2(Et_2dtc)_4]^+$ (1103); $[AgHgIr(Et_2dtc)_2(Pr_2dtc)_3]^+$ (1326); $[AgHgIr(Et_2dtc)_2(Pr_2dtc)_3S]^+$ (1358); $[AgIr_2(Pr_2dtc)_6]^+$ (1549); $[AgIr_2(Pr_2dtc)_6S]^+$ (1581); $[AgIr_2(Pr_2dtc)_6S_2]^+$ (1613)

that close to stoichiometric amounts of $Hg(R_2dtc)_2$ are required to effect the ligand-exchange reactions.

In sharp contrast to those of the cobalt systems, the ES mass spectrum of a mixture of $Rh(Et_2dtc)_3$, $Hg(Bu_2dtc)_2$, and $AgNO_3$ gave only three peaks due to $[AgRh_2(Et_2dtc)_6]^+$ (*m/z* 1203), $[AgRhHg(Et_2dtc)_3(Bu_2dtc)_2]^+$ (*m/z* 1264), and $[AgHg_2(Bu_2dtc)_4]^+$ (*m/z* 1327), showing that, in this case, global exchange does not occur but that the mixed-ligand silver cation is formed. These observations with the rhodium compound are as originally expected, but not observed, for the cobalt systems.

The reactions between $Ir(Pr_2dtc)_3$ and $Hg(Et_2dtc)_2$ in the presence of Ag(I) also yield unexpected results. A mixture of $Ir(Pr_2dtc)_3$, $Hg(Et_2dtc)_2$, and $AgNO_3$ (1:1:1) gave only very weak peaks due to $[AgHg_2(Et_2dtc)_4]^+$ (*m/z* 1103), $[AgHgIr(Et_2dtc)_2(Pr_2dtc)_3]^+$ (*m/z* 1326), and $[AgIr_2(Pr_2dtc)_6]^+$ (*m/z* 1549). However, much stronger peaks appeared at *m/z* 1358, 1581, and 1613, assigned to $[AgHgIr(Et_2dtc)_2(Pr_2dtc)_3S]^+$, $[AgIr_2(Pr_2dtc)_6S]^+$, and $[AgIr_2(Pr_2dtc)_6S_2]^+$, respectively. Similar sulfur-rich complexes have been observed previously as side products in the preparation of $[M_2(R_2dtc)_5]^+$ compounds. Maheu and Pignolet[31] isolated and characterized by X-ray crystallography $[Os_2(Et_2dtc)_3(Et_2dtcS)_2]^+$ (where Et_2dtcS represents diethyltrithiocarbamate), and similar species $[Co_2(R_2dtc)_5S]^+$ have also been detected by ESMS[16] in preparations of $[Co_2(R_2dtc)_5]^+$ made by oxidation of $Co(R_2dtc)_3$. The mechanism of formation of these products is not known, but oxidation of dithiocarbamates

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[31] Maheu, L. J.; Pignolet, L. H. *Inorg. Chem.* **1979**, *18*, 3626.

is always involved. Thus, in these systems, Ag(I) and $Hg(Et_2dtc)_2$ do not cause exchange of the dithiocarbamate ligands on iridium, but insertion of an extra sulfur atom occurs for at least two of the dithiocarbamates coordinated to iridium.

Reactions of Other Metal Dithiocarbamates with Ag(I). When $AgNO_3$ was reacted with $Zn(Pr_2dtc)_2$ and $Pb(Pr_2dtc)_2$, a different type of reaction occurred, and the ES mass spectra of the solutions showed peaks due to $[M_2(Pr_2dtc)_3]^+$ and $[M_3(Pr_2dtc)_5]^+$ (M = Zn, Pb). These ions are analogous to those of the same stoichiometries previously characterized for Hg(II) and Cd(II).[15] It is known that dithiocarbamate ligands are less strongly bound to lead than to mercury,[32] and a possible mechanism for formation of such a cation is

$$Pb(Pr_2dtc)_2 + Ag^+ \rightarrow [Pb(Pr_2dtc)]^+ + Ag(Pr_2dtc) \quad (1)$$

The cation then coordinates with excess $Pb(Pr_2dtc)_2$ to give $[Pb_2(Pr_2dtc)_3]^+$ (*m/z* 944) and $[Pb_3(Pr_2dtc)_5]^+$ (*m/z* 1503). Similarly, the zinc system gives peaks due to $[Zn_2(Pr_2dtc)_3]^+$ (*m/z* 660) and $[Zn_3(Pr_2dtc)_5]^+$ (*m/z* 1076). Presumably, this reaction does not occur with the mercury dithiocarbamates because the ligand is more strongly bound to mercury than to silver.

When $AgNO_3$ was reacted with $Fe(Et_2dtc)_3$ and $Ni(Et_2dtc)_2$, the ES mass spectra of the solutions showed that oxidation had occurred to give $[Fe(Et_2dtc)_3]^+$ and $[Ni(Et_2dtc)_3]^+$, which are the products formed by either electrochemical or chemical oxidation, so that in these cases Ag(I) is acting as an innocent oxidant. Both cations have been characterized previously by ESMS.[16] In the mixed acetonitrile/dichloromethane solvent system the E°_F value for the Ag^+/Ag redox couple is probably considerably more positive than that found in pure coordinating solvents such as acetonitrile by analogy with the redox couples of other metals,[33] so the ability of Ag^+ to act as either an oxidant or a coordinating metal, or both, is not surprising.

General Conclusions

There are several conclusions that can be made from this work. The first is that ESMS is a powerful method to explore new chemistry in solution. With this technique, it is easy to demonstrate ligand-exchange reactions in solution, and in favorable cases ESMS can distinguish between different exchange processes proceeding at different rates, such as the exchange of complete $Pt(R_2dtc)_2$ units on Ag(I) and the global scrambling of dithiocarbamates on Pt(II).

Metal dithiocarbamates have been studied for many years because they regularly provide new features of their chemistry. In recent years, the interest has been in redox properties and the ability of these ligands to stabilize high oxidation states of transition metals. The work of Kawamura and co-workers[13,14] on the $Ag/Pt(R_2dtc)_2$ complexes and our previous work on the mercury-rich dithiocarbamate cations indicated that some metal dithiocarbamates can act as ligands toward other metallic cations. The present study shows that this is a general phenomenon for several types of metal dithiocarbamate complexes and that there is an extensive chemistry of these types to be explored and confirmed by other techniques. Examples are now known where metal dithiocarbamates act as ligands toward several types of singly charged cations such as the bare metal (Ag^+), the $[M(R_2dtc)]^+$ cations (M = Hg, Cd, Zn, Pb), and the $[M'(R_2dtc)_2]^+$ cations (M' = Co, Rh, Os, etc.).

The observation of catalytic dithiocarbamate ligand exchange on both Pt(II) and Co(III) has interesting implications in the synthetic chemistry of metal dithiolates generally.

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(32) Bond, A. M.; Colton, R.; Hollenkamp, A. F. *Inorg. Chem.* **1990**, *29*, 1991.

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