Table II. Values of the Constants in Reaction 6

System: M, X, T	k_X, M^{-1} sec^{-1}	k_{H_2O}, M^{-1} sec^{-1}	K, M
Pd, Cl, 5°	0.34	6.7	9.4×10^{-3}
Pd, Br, 5°	0.34	13	6.0×10^{-3}
Pd, Cl, 25°	2.2	71	3.7×10^{-3}
Pd, Br, 25°	1.9	210	1.8×10^{-3}
Pt, Cl, 55°	1.2×10^{-3}	1.17×10^{-2}	2.3×10^{-2}
Pt, Br, 55°	1.08×10^{-3}	2.98×10^{-1}	1.5×10^{-3}

equilibrium between MX_4^{2-} and $M(H_2O)X_3^-$ is maintained throughout the kinetic run. When comparisons can be made with known aquation rates, the assumption has been shown to be justified.[9] A few kinetic runs showed small deviations at the very beginning as the equilibrium was being established. Reaction constants were calculated from the observed rate constants and their corresponding halide concentrations. Initially, two values of k_{obsd} at small $[X^-]$ were substituted into eq 7 to solve for k_X, neglecting the $k_{H_2O}K$ term. Crude values for k_{H_2O} and K were then obtained from two values of k_{obsd} at large $[X^-]$ and the number that had been calculated for k_X. These values were used to improve the calculation of k_X, and so on. A few such cycles of calculation gave a convergent solution. Minor adjustments in the reaction constants were then made by trial and error to provide the nearest correspondence between k_{obsd} and k_{calcd} throughout the range of $[X^-]$. Reaction constants are given in Table II. A number of comparisons may be made among the reaction constants. When adjusted to 55°, palladium reactions were faster than corresponding platinum reactions by factors of 2×10^4 to 10^5. Other workers[20] find similar factors and ascribe them to weaker palladium bonds. $M(H_2O)X_3^-$ complexes were more reactive then MX_4^{2-} complexes, probably because water, a better leaving group than halide,[21] was expelled in the $M(H_2O)X_3^-$ reactions. Among the reactions of $M(H_2O)X_3^-$, those with X = Br were faster than those with X = Cl, because of the greater trans effect of bromide.[22] The similar MX_4^{2-} rates were the result of two opposing effects: bromide was a better trans labilizer but a poorer leaving group then chloride.

The equilibrium constants calculated from kinetics data may be compared with those derived by more direct measurements. No attempt was made to force the calculations of K to agree with published values. The constant for the first aquation step of $PtCl_4^{2-}$ at 55° is 2.5×10^{-2} M by an equilibrium method[9] and 2.3×10^{-2} M from kinetics. The constants at 25° for $PdCl_4^{2-}$ are 4×10^{-3} M (equilibrium,[23] corrected to $\mu = 0.278\,M$) and 3.7×10^{-3} M (kinetics). An attempt to measure the equilibrium constant for $PtBr_4^{2-}$ was not successful. In general it may be concluded that the bromide complexes follow the pattern of the chlorides in having a second-order solvent route to the product.

Very little can be concluded about the iodide complexes. Their reactions were much faster than those of chloride or bromide, but the form of the complex existing in solution was uncertain. The very insoluble $M(phen)I_2$ complexes seemed to precipitate more slowly than the rate at which phenanthroline was used up, suggesting that the initial substitution product might have been something like $M(H_2O)(phen)I^+$.

Registry No. Phen, 66-71-7; $PdCl_4^{2-}$, 14349-67-8; $Pd(phen)Cl_2$, 14783-10-9; $PdBr_4^{2-}$, 14127-70-9; $Pd(phen)Br_2$, 41876-11-3; PdI_4^{2-}, 16182-47-1; $Pd(phen)I_2$, 41876-12-4; $PtCl_4^{2-}$, 13965-91-8; $Pt(phen)Cl_2$, 18432-95-6; $PtBr_4^{2-}$, 14493-01-7; $Pt(phen)Br_2$, 42847-12-1; PtI_4^{2-}, 14349-66-7; $Pt(phen)I_2$, 42847-13-2.

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Contribution from the William Rand Kenan, Jr.,
Laboratories of Chemistry, University of North Carolina,
Chapel Hill, North Carolina 27514

Unusual Magnetic Properties of Polymeric Cobalt(II) Monoglycerolate, a Compound Containing Alkoxo-Bridged Cobalt(II) Ions

Richard P. Eckberg, William E. Hatfield,* and D. Bruce Losee

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Complex compounds of various transition metal ions with glycerine have been known for several years.[1] The structure of one of these, cobalt(II) monoglycerolate, $[Co(C_3H_6O_3)]_n$, has been found[2] to be a two-dimensional polymer. The magnetic moment observed at room temperature for this complex, 3.94 BM,[1] is lower than usually observed for high-spin cobalt(II). This fact, coupled with the unusual magnetic properties which are often characteristic of polymeric transition metal complexes, have made cobalt(II) monoglycerolate a subject of interest for low-temperature magnetic susceptibility studies. The results of our measurements in the temperature range 1.6–50°K are described in this note.

Experimental Section

The compound was prepared by heating a mixture of 10.0 g of cobalt(II) acetate in 100 ml of 96% glycerine (U. S. Pharmacopoeia grade) with constant stirring, to a temperature of 165° for 60 hr. The crude product was filtered from the resulting suspension, washed repeatedly with water, ethanol, and ether, and dried *in vacuo* at 110° for 24 hr. The resulting product was a deep magenta, finely divided powder which was insoluble in all common solvents.

Anal. Calcd for $[Co(C_3H_6O_3)]_n$: C, 24.18; H, 4.06; Co, 39.55. Found: C, 24.33; H, 3.95; Co, 39.77.

Attempts to obtain crystals large enough for single-crystal susceptibility measurements have thus far been unsuccessful. The insolubility of the material in all solvents tested ruled out crystal growth *via* slow evaporation from solution. Crystal growth in a silica gel[3] has been attempted but the high temperature required for reaction between glycerine and cobalt acetate has to date prevented the slow dispersion of the reactants along the gel–aqueous interface from producing the desired crystalline product at temperatures low enough to prevent evaporation of the aqueous phase. Therefore, magnetic susceptibility measurements have been confined to powder specimens. The magnetic susceptibility measurements were made with a PAR vibrating-sample magnetometer[4] which is capable of operating over a wide range of field strengths. The magnetometer was calibrated with $HgCo(NCS)_4$,[5] and temperatures were measured using a calibrated gallium arsenide diode.

Although epr g values have been reported for Co(II) in a five-coordinate environment at 77°K,[6] all attempts at observing an epr signal at 77°K failed for cobalt monoglycerolate.

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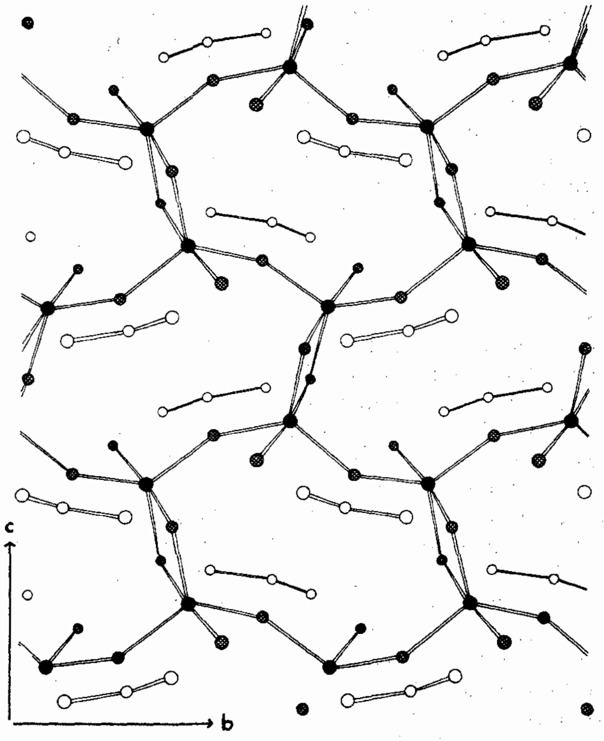

Figure 1. A view of the crystal structure of $[Co(C_3H_6O_3)]_n$ along the *a* axis which illustrates the two-dimensional nature of the polymer. Cobalt atoms are shown as solid circles, carbon atoms are open circles, and oxygen atoms are displayed as cross-hatched circles. Carbon–oxygen bonds are omitted for clarity.

Results and Discussion

The polymeric structure of the complex, as determined by X-ray diffraction,[2] is very unusual. Cobalt is five-coordinate and bonded in a highly distorted trigonal-bipyramidal arrangement to oxygen. An infinite chain of cobalt atoms (Co–Co distance approximately equal to 3.6 Å) joined by singly bridging alkoxide oxygen atoms roughly parallels the crystallographic *b* axis. As shown in Figure 1, these chains are linked along the *c* axis by four-membered alkoxide bridges, Co–Co = 3.1 Å, effectively forming two-dimensional polymeric sheets in the *bc* plane. These features are illustrated in Figures 1 and 2. The relative isolation of these sheets is shown in Figure 2 where it may be seen that the carbon–hydrogen backbone of the glycerine molecules effectively separate the cobalt(II) ions in adjacent two-dimensional layers by more than 8 Å along the crystallographic *a* axis.

The magnetic susceptibility was measured between 1.6 and 50°K at several field strengths on a finely ground sample of the material. The data obtained at 10 kG which are shown in Figure 3 reveal a sharp increase in susceptibility below 40°K with a nearly constant temperature-independent susceptibility persisting to the lowest temperature achieved. When the data were collected at 100 G, a profound change in the magnetic properties occurred; this is also shown in Figure 3. There is a sharp rise at 37°K but at approximately 35.5°K there is an extremely sharp drop in magnetic susceptibility to a value which is approximately one-tenth of the value at the maximum. Such behavior suggests a phase transition to an antiferromagnetic state. The susceptibility, as expected for an antiferromagnet, is temperature independent until 20°K where there is a gradual rise in the susceptibility with some leveling off at the lowest temperatures. The susceptibility above 40°K is found to be nearly field independent while the data at or just below the transition temperature are found to be still dependent upon the field and there is no reason to suspect that the measured susceptibilities are those that would be measured in "near-zero field." As might be expected, the measurement of the susceptibility in the temperature range of 1.6–36°K displayed significant hysteresis. These observations, along with the exceptionally sharp rise in the susceptibility close to the transition temperature, are suggestive of the behavior one might expect for a canted antiferromagnet. In this regard Moriya[7] has shown that a canted spin arrangement is strictly forbidden between transition metal ions if an inversion center lies between these ions. Such an inversion center is present between the cobalt ions which are doubly bridged by the alkoxide linkages. However, on symmetry grounds the interaction is allowed between the singly bridged cobalt ions infinitely extended in the *b* direction. Of course, until single-crystal measurements can be made on this compound at "near-zero field" the

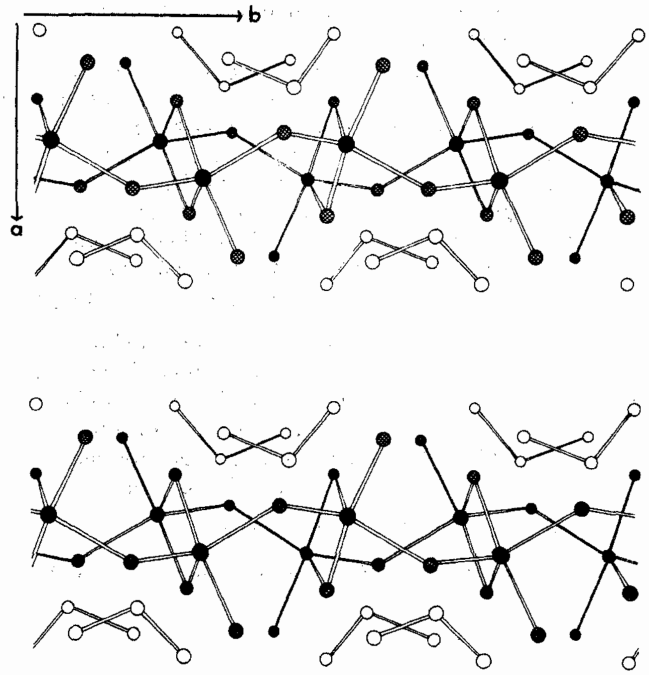

Figure 2. A view of the crystal structure of $[Co(C_3H_6O_3)]_n$ along the *c* axis which illustrates the separation of the two-dimensional layers.

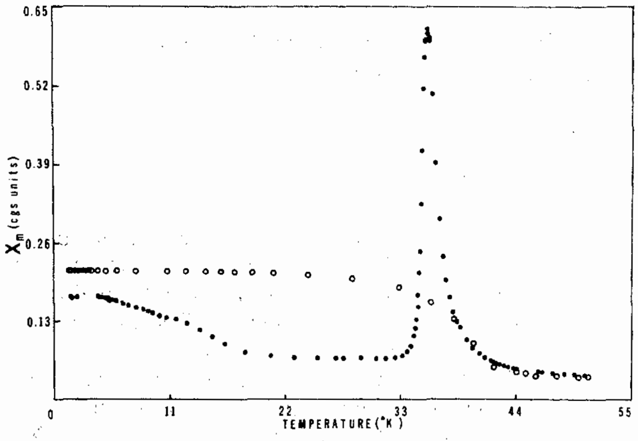

Figure 3. The experimental magnetic susceptibilities of a powdered sample of $[Co(C_3H_6O_3)]_n$ from 1.6 to 55°K. Solid circles are susceptibilities taken at a field strength of 100 G, and open circles are susceptibilities measured at a field strength of 10,000 G.

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detailed picture of the magnetic behavior can be but a reasonable speculation.

The low-temperature behavior (*i.e.*, below 20°K) is highly unusual. Presumably, in this temperature region, the material has ordered antiferromagnetically. Although this behavior may be due to an impurity, it is improbable that it is due to unreacted cobalt acetate since this material has been shown to be paramagnetic to 0.4°K.[8] As mentioned above, the magnetic susceptibility in this region is still field dependent and the observed behavior may be due to a spin reorientation which is affected by the small measuring field of the magnet.

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Contribution from the Edward Davies Chemical Laboratories,
University College of Wales, Aberystwyth, United Kingdom

X-Ray Photoelectron Spectroscopic Studies of Halide Complexes of Antimony(III)

M. J. Tricker

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It is well known that binding energies of core levels are affected by changes in the valence shell of electrons and that these changes as measured by XPS can yield information on chemical bonding.[1] We report here an XPS study of a number of halide complexes of antimony. The complexes $M_3Sb_2X_9$ (M = alkali metal; X = Cl, Br, I) studied are virtually isostructural and contain antimony(III) in a halogen coordination close to octahedral.[2,3] $Co(NH_3)_6SbX_6$ complexes (X = Br, Cl) also contain six-coordinate antimony(III)[2-4] and consequently the differences in lattice potentials due to the distribution of charge in the lattice are hopefully minimized in this series of compounds. The fluoroantimonates(III) have more complex structures and these structures will be discussed in more detail later.

Results

The measured binding energy of the antimony 3d spin-orbit doublet and representative alkali metal and halogen core levels are presented in Table I. The antimony 3d levels are strong and consist of a well-separated spin-orbit doublet (9.3 ± 0.2 eV). The full widths at half-maximum height (FWHM) vary from 1.5 to 2.2 eV and the peak maxima were located with a precision of 0.1 eV. The binding energies presented are referenced against the C 1s contaminant line taken as 285 eV. [No attempt to correct for lattice potential effects by using an internal reference[5] (such as F 1s) has been made. This procedure is clearly incorrect for materials of differing structure and also incorrect for crystal structures with more than one site where lattice potentials can be different at each site.] The antimony 3d binding energies range from 539.3 and 530.1 eV for the 3d$_{3/2}$ and 3d$_{5/2}$ levels of $Rb_3Sb_2I_9$ to 540.8 and 531.5 eV for Na_2SbF_5, a spread of 1.5 eV.

Discussion

The measured 3d binding energies of the antimony(III) halides show a gross trend with ligand electronegativity; in general the fluoride-containing materials have the highest and the iodides the lowest antimony 3d binding energies. This is the expected result for decreasing ionicity of the antimony-halogen bond in going from Sb-F to Sb-I if the dominant term contributing to the total shift is the valence term. It has been demonstrated that for closely related series of compounds, *e.g.*, the series Y_2Sn(8-quinolinato)$_2$, where Y = Et, Ph, or halogen[6] and mixed hexahalides of tin(IV),[7] a correlation is observed between Mossbauer isomer shifts and XPS chemical shifts. Further a correlation between ^{57}Fe Mossbauer isomer shift and the iron 2p$_{1/2}$, 2p$_{3/2}$ binding energies of a series of low-spin ferrous complexes has been observed.[8] The ^{121}Sb Mossbauer chemical shifts of the six-coordinate antimony(III) materials studied demonstrate[9] a large 5s character of the Sb(III) lone-pair orbital and also reflect the electrostatic nature of the antimony-halogen bond.[3] A reasonable correlation is found, for the chloride, bromides, and iodides studied, between the measured 3d binding energies and Mossbauer chemical shifts (Figure 1). However the parameters for the fluoroantimonates(III) do not fall on the same line. The Mossbauer isomer shift is determined by the total s-electron density at the nucleus, whereas the XPS chemical shifts are sensitive to change in population of all valence orbitals on the metal. Consequently for a series of materials where significant and varying 5s-5p mixing occurs as in the fluoroantimonates(III)[10] no correlation between Mossbauer and XPS chemical shifts can be expected. A linear correlation between Mossbauer and XPS chemical shifts for the chloride-, bromide-, and iodide-antimony(III) complexes implies therefore that the 5s character of the antimony lone pair is similar in all the materials, and changes in the Mossbauer isomer shift are brought about directly by any changes in residual 5s character of the antimony-halogen bonds and indirectly by shielding of 5s antimony electrons by antimony 5p electrons.

The antimony 3d spectra of the fluoride complexes have slightly larger line widths than the other halide materials studied, but all three fluorides have similar line widths. The crystal structure[11] of K_2SbF_5 contains crystallographically equivalent antimony atoms and two groups of four equivalent fluorines in difference crystallographic sites resulting in an

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