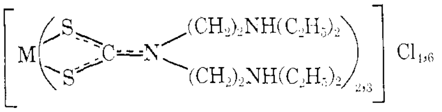
coordination of the tertiary nitrogen atoms. This is not surprising in view of the low tendency of planar dithiocarbamate complexes to form adducts with nitrogenous bases[14] and in view of the poor coordinative properties of monodentate, tertiary amines.[16]

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 $(S_2^-)C{\cdots}N^+R_2$.[8,14,15] It should be pointed out that the C$\cdots$N bands are sharp in the electrolytes, whereas the C$\cdots$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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[16] J. C. Bailar, Jr., and D. H. Busch, "Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., American Chemical Society Monograph No. 131, Reinhold Publishing Corp., New York, N. Y., p 62.

[17] M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, p 524.

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

BY THOMAS G. SPIRO, VICTOR A. MARONI,
AND CARL O. QUICKSALL

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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.

[2] V. A. Maroni and T. G. Spiro, *J. Am. Chem. Soc.*, **89**, 45 (1967).

[3] V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, **7**, 188 (1968).

[4] V. A. Maroni and T. G. Spiro, *ibid.*, **7**, 183 (1968).

[5] T. G. Spiro, D. H. Templeton, and A. Zalkin, *ibid.*, **8**, 856 (1969).

While a discrete hexanuclear complex is indeed found, the lead atoms are not arranged in an octahedron, but rather in three face-sharing tetrahedra as shown in Figure 1. Furthermore the complex contains not eight oxygens but seven and should be formulated $Pb_6O(OH)_6^{4+}$. The unique oxygen is found at the center of the central lead tetrahedron, while the six hydroxide groups cover the six exterior faces of the two exterior tetrahedra. The adjacent lead–lead distances are quite varied, ranging from about 4.0 Å for the edges of the diamond-shaped base of the complex down to 3.44 Å for the unique interaction between the two lead atoms (Pb(3) and Pb(4) in Figure 1) each of which has five nearest neighbor lead atoms. The latter distance is 0.06 Å shorter than the internuclear distance in metallic lead. Interestingly, the unusual structure of this complex is apparently retained in aqueous solution, as indicated by the solution X-ray scattering results of Johansson and Olin.[6]

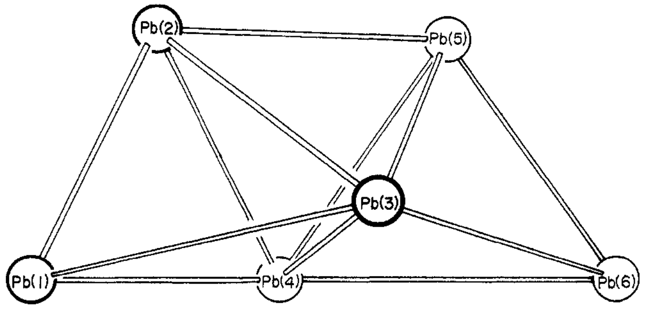

Figure 1.—The arrangement of lead atoms in $Pb_6O(OH)_6^{4+}$.[5] For distances see Table I.

The idealized symmetry of $Pb_6O(OH)_6^{4+}$ is C_2. There are twelve lead–lead interactions, and one expects twelve "cluster" type modes, instead of the three predicted for octahedral symmetry. Examination of our Raman spectrum (Figure 1C of ref 2), obtained on a microcrystalline sample using mercury arc (4358 Å) exciting radiation and a spectral slit width of 10 cm^{-1}, shows that while the highest of the three low-frequency bands is strong and sharp, the other two are quite broad and are superimposed on the rising background from the exciting line. In retrospect it is not altogether surprising that they might hide considerable complexity in the spectrum.

Results

We have now reexamined the low-frequency Raman spectrum of $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$, using He–Ne (6328 Å) laser excitation and a single crystal cooled to about −110° in a stream of cold nitrogen. The result is shown in Figure 2. The highest band moves 6 cm^{-1} to higher frequency but remains unsplit. The Raman emission below 130 cm^{-1} is now resolved into a number of features: three medium-intensity bands and at least five weak ones.[7] Reducing the spectral slit width below 3 cm^{-1} had no effect on the resolution. The spectrum no longer bears any resemblance to that expected for an octahedral cluster. The dangers of inferring symmetrical structures from inadequately resolved vibrational spectra are clearly illustrated in this case.

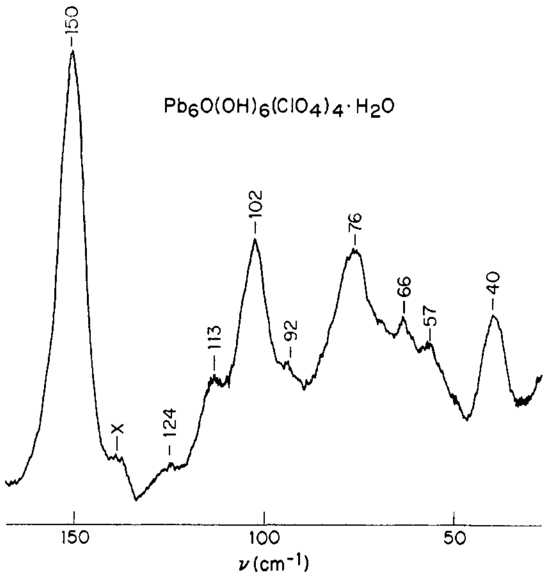

Figure 2.—Low-frequency Raman spectrum of a single crystal (~2 mm per edge cube, arbitrary mounting) of $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$, cooled to about −110° in a stream of cold nitrogen. Conditions: 6328-Å He–Ne laser excitation (unfiltered); scattered light collected at 90°; slit width 3.1 cm^{-1} (double monochromator); time constant 10 sec; scan rate 10 cm^{-1}/min. The feature marked X in the spectrum is a neon discharge line at 6383 Å.

It seemed of interest to determine to what extent a simple cluster model, based on the known arrangement of the lead atoms, can still account for the observed frequencies. In this model all ligands are neglected and stretch–stretch interaction constants for the cluster atoms are ignored. For an octahedral cluster all nearest neighbor distances are equal and only one primary force constant is needed. For the lead atom arrangement in $Pb_6O(OH)_6^{4+}$ (Figure 1) there are several nearest neighbor distances, and it seems reasonable that they should be assigned different force constants. The force constants should, however, be related by Badger's rule.[8]

A calculation was carried out as follows. The complex was assumed to have C_2 symmetry. The lead–lead distances can be grouped into five sets whose members are nearly equal, as shown in Table I. The *G* matrix for this arrangement of lead atoms was constructed by the method of Wilson, *et al.*,[9] with the aid of

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[6] G. Johansson and A. Olin, *Acta Chem. Scand.*, **22**, 3197 (1969).

[7] There is no evidence for a phase change; both frequency shift and band resolution occurred gradually on cooling. The crystal orientation is not critical since the complex is of low symmetry. Qualitative examination with a polarizing microscope indicated that the crystal was mounted on a diagonal of one of the unit cell (orthorhombic Pbca[6]) faces.

[8] R. M. Badger, *J. Chem. Phys.*, **3**, 710 (1935).

[9] E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

Schachtschneider's program GMAT.[10] Each of the five sets of Pb–Pb bonds was assigned a force constant and the F matrix was constructed. The G and F matrices were factored using C_2 symmetry coordinates constructed by standard group theoretical methods. The secular equation was solved using Schachtschneider's program FPERT.[10]

It was assumed the highest frequency mode, at 150 cm^{-1}, arises primarily from the short unique Pb(3)–Pb(4) interaction of 3.44 Å. An initial value of $f_{\mathrm{Pb(3)-Pb(4)}}$ was estimated from the 150-cm^{-1} frequency and the diagonal G matrix element. This force constant was then used to evaluate the d_{ij} parameter in Badger's equation

$$r = d_{ij} + (c_{ij}/f)^{1/3}$$

where r is the internuclear distance, in ångströms, and f is the force constant in megadynes per centimeter. The parameter c_{ij} is about 0.5 for all heavy atoms, and its value is not critical in the calculation. Using the Pb(3)–Pb(4) distance and force constant, we obtained d_{ij} = 2.40 Å and used this value to determine the other Pb–Pb force constants. With these values held constant, $f_{\mathrm{Pb(3)-Pb(4)}}$ was then adjusted to calculate the 150-cm^{-1} frequency exactly. The small change in $f_{\mathrm{Pb(3)-Pb(4)}}$ required an insignificant change in d_{ij}. In this way all five force constants were fixed with one adjustable parameter. Their values are listed in Table I.

TABLE I

LEAD–LEAD DISTANCES AND ASSUMED FORCE CONSTANTS IN $Pb_6O(OH)_6^{4+}$

Interaction (see Figure 1)	Crystallographic distance, Å	Assumed distance (C_2 model)	$f_{\mathrm{Pb-Pb}}$, mdyn/Å
Pb(3)–Pb(4)	3.44	3.44	1.09
Pb(5)–Pb(6)	3.67	3.67	0.62
Pb(1)–Pb(2)	3.67		
Pb(4)–Pb(5)	3.78	3.79	0.48
Pb(3)–Pb(5)	3.78		
Pb(2)–Pb(4)	3.79		
Pb(2)–Pb(5)	3.79		
Pb(2)–Pb(3)	3.80		
Pb(3)–Pb(6)	3.85	3.90	0.37
Pb(1)–Pb(4)	3.95		
Pb(1)–Pb(3)	4.09	4.09	0.26
Pb(4)–Pb(6)	4.09		

The twelve fundamental frequencies calculated by this set of force constants are compared with the observed frequencies in Table II. Considering the crudeness of the model, the over-all match is surprisingly good. It is clear that all of the frequencies could be calculated exactly by adjusting the individual Pb–Pb force constants within a reasonable range. The resulting values would have little significance, of course, since the actual force field must be vastly more complex than our model allows for. Our purpose here is merely to show that the resolved low-frequency Raman spectrum of $Pb_6O(OH)_6^{4+}$ is a reasonable consequence, within the simple cluster framework, of the actual arrangement of the lead atoms, taken together with Badger's rule.

TABLE II

LOW-FREQUENCY VIBRATIONS (CM^{-1}) FOR $Pb_6O(OH)_6^{4+}$

Obsd	Calcd	Symmetry type (C_2)	Obsd	Calcd	Symmetry type (C_2)
150	150	A	76	83	B
124	120	B	66	74	B
113	113	A	57	68	A
102	108	A	. . .	43	B
92	87	A	40	41	A
. . .	87	B	. . .	36	A

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Spectra of Cobalt(II) and Nickel(II) in Acetate Melts

BY R. A. BAILEY, M. ELGUINDY, AND J. A. WALDEN

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The coordination geometry around transition metal ions dissolved in fused salts has been the subject of considerable interest.[1,2] The behavior of Co(II) in such media is particularly interesting, as both tetrahedral and octahedral geometries can be observed. Co(II) has been investigated extensively in fused halide media and to a lesser degree in oxy anion melts. In fused nitrates, Gruen[1,3,4] interpreted the spectrum on the basis of an octahedral species, while in fused sulfates, Johnson and Piper considered Co(II) to be tetrahedrally surrounded.[5] In both cases, interpretations were based chiefly on the band in the 18,000-cm^{-1} range, which is structured and can be ambiguous. In addition, extinction coefficients in both systems (in units of 1000 cm^2 M^{-1}) were *ca.* 100; compared to typical octahedral values near 10 and tetrahedral values near 500 for this ion with other ligand species.[1] Nickel(II) was octahedral in both of the above melts.[4,5] This report deals with further observations of Co(II) and Ni(II) in oxy anion melts, *i.e.*, molten acetates.

Experimental Section

Melt spectra were taken in stoppered quartz cells using a Unicam SP700 spectrophotometer and the heated cell compartment described previously.[6] Reflectance spectra were taken on a Beckman DU spectrophotometer equipped with a diffuse reflectance attachment and using powdered $MgCO_3$ as reference.

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[10] J. H. Schachtschneider, Technical Reports No. 231-64 and No. 57-65, Shell Development Co., Emeryville, Calif.

(1) D. M. Gruen in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

(2) G. P. Smith in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, New York, N. Y., 1964.

(3) D. M. Gruen, *Nature*, **178**, 1181 (1956).

(4) D. M. Gruen, *J. Inorg. Nucl. Chem.*, **4**, 74 (1957).

(5) K. E. Johnson and T. S. Piper, *Discussions Faraday Soc.*, **32**, 32 (1962).

(6) R. A. Bailey and J. A. McIntyre, *Rev. Sci. Instr.*, **36**, 968 (1965).