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Crystal and Molecular Structure of a Cryptate Complex of Samarium: $C_{18}H_{36}O_6N_2Sm_2(NO_3)_6 \cdot H_2O$

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A compound made by reacting $Sm(NO_3)_3$ with the cryptand designated [2.2.2] was analyzed by single-crystal X-ray diffraction to determine its composition, $C_{18}H_{36}O_6N_2Sm_2(NO_3)_6 \cdot H_2O$, and its molecular structure. The triclinic unit cell has $a = 14.815$ (3) Å, $b = 8.813$ (1) Å, $c = 13.253$ (3) Å, $\alpha = 91.51$ (2)°, $\beta = 92.48$ (2)°, and $\gamma = 86.73$ (2)°; the space group is $P\bar{1}$ and $Z = 2$. The structure was determined by the heavy-atom method and refined by least squares. Positions and anisotropic thermal parameters of the 53 independent nonhydrogen atoms of the asymmetric unit were adjusted until the agreement factor, R_F , reached 0.038 for 6941 observations. The crystal contains two complex ions: $[Sm[2.2.2]NO_3]^{2+}$ and $[Sm(NO_3)_5 \cdot H_2O]^{2-}$. In the complex cation the Sm^{3+} ion is enclosed in the bicyclic ligand and is bonded to its six O atoms and two N atoms as well as to a bidentate NO_3^- ion inserted between strands of the ligand. Considerable distortion of the ligand from its conformation in the uncomplexed state is observed. The complex anion has five bidentate NO_3^- ions and a water molecule surrounding a Sm^{3+} ion. There are no especially close contacts between ions other than for some weak hydrogen bonds.

Introduction

Structural studies have had an important role in obtaining an understanding of the behavior of macropolycyclic inclusion complexes, the so-named "cryptates" of Lehn.¹ One finding has been that the strength of complexation of various mono- and divalent cations by these ligands (cryptands) is strongly dependent on the matching of the size of the included ion to that of the cryptand cavity. The numerous crystal-structure determinations supportive of this conclusion were done mainly by Weiss and co-workers.²

Recently, work has been extended to include ions of higher valence, and preliminary reports on lanthanide³ and U(IV)⁴ complexes have appeared. Samarium(III) was used in the present work because it is a typical lanthanide element and because its ionic radius is near that of the trivalent transuranic elements for which it can often be used as a nonradioactive substitute in chemical studies.⁵ After this work was in progress, two reports of related crystal structures appeared, that of $[(C_{18}H_{36}O_6N_2La(NO_3)_2)_3[La(NO_3)_6] \cdot 2CH_3OH]^6$ and of $[(C_{18}H_{36}O_6N_2)EuClO_4](ClO_4)_2 \cdot CH_3CN$.⁷ Taken together, these three reports provide a basis for understanding of how one cryptand, namely, [2.2.2],⁸ complexes with the lighter lanthanide elements.

Experimental Section

Preparation of the Compound. Samarium nitrate hexahydrate, obtained by dissolution of Sm metal (Fairmount Chemical Co., Inc.) in HNO_3 , was dissolved in CH_3CN and refluxed 24 h over molecular sieves to remove all but a trace of water. This solution was mixed with twice the stoichiometric amount of [2.2.2] ligand (PCR Research Chemicals, Inc.) dissolved in CH_3CN . Some precipitate formed immediately, but more came out overnight and included some large, pale yellow, prismatic crystals. These large ones were used for the structure analysis, but at least two other crystalline solids were found to be present and distinguished by X-ray precession photography; these were not characterized further. Conventional chemical analysis was not employed on the compound of interest, but structure determination established its formula to be $(C_{18}H_{36}O_6N_2)_2Sm_2(NO_3)_6 \cdot H_2O$.

X-ray Diffraction. X-ray precession photographs were used to establish that the lattice is triclinic and to provide provisional values for the unit-cell dimensions. By flotation d_{meas} is 2.06 g cm^{-3} ; and with two of the formula units written above in the unit cell, d_{calc} is 2.05 g cm^{-3} . A center of symmetry was assumed, making the space group $P\bar{1}$, and the precision of the refinement eventually attained indicates that this is correct.

For accurate measurement of the unit cell and the collection of intensity data a pentagonal-prismatic crystal specimen, having dimensions of about 0.025 cm on a pentagonal edge and a length of about 0.045 cm, was mounted on a Picker four-circle goniometer.

Twelve reflections in the 2θ range of 49–55° were carefully centered, and their angular settings were used to obtain the best estimate of the unit-cell dimensions⁹ by the method of least squares. At 23 °C, these are $a = 14.815$ (3) Å, $b = 8.813$ (1) Å, $c = 13.253$ (3) Å, $\alpha = 91.51$ (2)°, $\beta = 92.48$ (2)°, and $\gamma = 86.73$ (2)°. Intensity data were obtained automatically under computer control, and a reference reflection was measured hourly. The reference intensity gradually dropped by a total of 3.6% over 3 weeks of data collection. X-rays used were Mo $K\alpha$ (Zr filtered) at 2.5° takeoff angle; a scintillation detector was located behind a 0.6 cm square aperture 21 cm from the sample. The θ - 2θ scanning technique was used, and the background was estimated by averaging counts made at the ends of each scan. Lengths of scans varied from 0.8° at $2\theta = 2.5^\circ$ up to 1.55° at $2\theta = 55^\circ$, the maximum of the scan range. All reflections in half the reciprocal sphere up to this limit were recorded.

Structure Determination and Refinement

Data Reduction. The shape of the crystal specimen was measured with a microscope, and the boundary planes were used in the calculation¹¹ of transmission factors for all reflections. Because the chemical composition was not known initially, the linear absorption coefficient, μ , was estimated; but after the structure was determined, transmission factors were recalculated by using the correct value, $\mu = 32.8 \text{ cm}^{-1}$. The transmission factors, ranging from 0.29 to 0.40, as well as Lorentz and polarization corrections were applied to the counting data. They were also normalized by a factor based on interpolation between measurements of the reference reflection. This data reduction yielded a set of relative squared structure factors, F_o^2 ; their variances, $\sigma^2(F_o^2)$, were taken to be equal to $\sigma_c^2 + (0.05F_o^2)^2$, where σ_c^2 is the variance attributable to counting statistics and the second contribution represents systematic errors.

Structure Determination. A Patterson map was calculated, and its prominent maxima were interpreted in terms of vectors between two independent Sm atoms located in general positions of $P\bar{1}$. Subsequent electron-density maps, using phases calculated from the contributions of these two Sm atoms, reveal the location of the C, N, and O atoms. At this point the exact formula of the compound was first known. There are 53 nonhydrogen atoms in the asymmetric unit; all are in general positions. Hydrogen atoms were neither found nor included in the calculations.

Refinement. Atomic coordinates and anisotropic thermal parameters for all atoms were refined by the method of least squares. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, in which $w = 1/\sigma^2(F_o^2)$ and F_c is the calculated structure factor. In the calculation of F_c , scattering factors¹² for neutral atoms were used, with anomalous dispersion corrections¹³ applied for Sm. Of the 7644 reflections measured, those 6941 with $F_o^2 > 3\sigma(F_o^2)$ were included in the refinement. Convergence was smooth, and the agreement index, $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$, reached 0.038; $\sigma_1 = 1.65$.

Refined atomic coordinates are listed in Table I, and anisotropic thermal parameters are given in Table II.

Table I. Atomic Coordinates and Standard Deviations

atom	10 ⁴ x	10 ⁴ y	10 ⁴ z
Sm(1)	2026.9 (2)	8697.7 (2)	6924.5 (2)
Sm(2)	3168.3 (2)	4471.8 (3)	1857.8 (2)
O(1)	3106 (3)	9208 (5)	8376 (3)
O(2)	1398 (4)	9899 (6)	8553 (4)
O(3)	3081 (3)	6533 (4)	6585 (3)
O(4)	1900 (4)	6387 (5)	7916 (4)
O(5)	2338 (4)	9116 (6)	5088 (3)
O(6)	1077 (4)	7377 (6)	5641 (5)
O(7)	3570 (3)	6471 (4)	3170 (3)
O(8)	4674 (2)	5008 (4)	2682 (3)
O(9)	4923 (3)	6775 (5)	3809 (4)
O(10)	4603 (3)	3876 (5)	736 (3)
O(11)	3280 (3)	3490 (5)	71 (3)
O(12)	4468 (4)	2843 (6)	-766 (4)
O(13)	3843 (3)	1701 (5)	1828 (4)
O(14)	2394 (3)	1962 (5)	1797 (3)
O(15)	3040 (5)	-290 (5)	1834 (5)
O(16)	3314 (3)	3321 (5)	3611 (3)
O(17)	2031 (3)	4452 (5)	3232 (3)
O(18)	2236 (4)	3403 (6)	4678 (4)
O(19)	1964 (3)	6758 (5)	1835 (4)
O(20)	1661 (3)	4764 (6)	952 (4)
O(21)	664 (4)	6591 (8)	1056 (5)
O(22)	2113 (3)	11526 (4)	6966 (3)
O(23)	911 (3)	10677 (4)	6262 (3)
O(24)	991 (3)	13087 (5)	6574 (4)
O(w)	3641 (3)	6729 (4)	961 (3)
N(1)	3745 (3)	9339 (5)	6431 (4)
N(2)	313 (4)	8015 (8)	7485 (7)
N(3)	4404 (3)	6110 (5)	3233 (3)
N(4)	4126 (3)	3393 (5)	3 (4)
N(5)	3090 (4)	1087 (5)	1823 (4)
N(6)	2520 (4)	3718 (5)	3858 (4)
N(7)	1407 (4)	6069 (7)	1278 (4)
N(8)	1325 (3)	11823 (5)	6596 (3)
C(1)	4202 (5)	10102 (7)	7299 (7)
C(2)	4082 (5)	9236 (10)	8216 (7)
C(3)	2823 (9)	9877 (18)	9263 (7)
C(4)	1967 (9)	10416 (15)	9347 (6)
C(5)	513 (8)	9988 (15)	8864 (9)
C(6)	-93 (6)	9425 (12)	8012 (11)
C(7)	4310 (5)	7942 (7)	6120 (6)
C(8)	3742 (3)	6643 (6)	5800 (5)
C(9)	2999 (4)	5044 (6)	6978 (5)
C(10)	2659 (6)	5298 (8)	7998 (6)
C(11)	1158 (7)	6175 (11)	8530 (7)
C(12)	299 (7)	6669 (14)	8098 (13)
C(13)	3637 (6)	10440 (8)	5597 (7)
C(14)	3120 (7)	9783 (9)	4708 (6)
C(15)	1685 (11)	8491 (14)	4314 (6)
C(16)	1314 (11)	7102 (18)	4708 (11)
C(17)	202 (11)	6834 (17)	5851 (11)
C(18)	-208 (7)	7669 (18)	6574 (17)

Description and Discussion of the Structure

The crystal structure is composed of cations, $(C_{18}H_{36}O_6N_2SmNO_3)^{2+}$, and anions, $[Sm(NO_3)_5 \cdot H_2O]^{2-}$, shown in Figure 1. These are packed in a fashion typical of ionic crystals, as can be seen in Figure 2 which depicts one unit cell of the structure. Bond lengths are compiled in Table III.

Of special interest is the complex cation, in which one Sm^{3+} ion is enclosed in a [2.2.2] molecule, forming a cryptate. The cryptand is in the in-in conformation, and all its heteroatoms are bonded to the Sm atom. In addition, one NO_3^- ion resides between two strands of the cryptand molecule and two of its O atoms are part of the coordination of the Sm atom. The coordination polyhedron can be described as a slightly irregular antiprism of O atoms capped on its "square" faces by N atoms. The best plane through atoms O(1), O(3), O(5), and O(22), which comprise one face of the antiprism, makes a dihedral

Table II. Anisotropic Thermal Parameters^a and Standard Deviations

Atom	10 ⁴ ε ₁₁	10 ⁴ ε ₂₂	10 ⁴ ε ₃₃	10 ⁴ ε ₁₂	10 ⁴ ε ₁₃	10 ⁴ ε ₂₃
Sm(1)	25.7(1)	61.3(3)	38.5(2)	-3.3(2)	-0.6(1)	1.2(2)
Sm(2)	25.6(1)	67.2(3)	44.8(2)	-4.6(2)	1.9(1)	0.8(2)
O(1)	62(3)	156(7)	68(3)	4(3)	-20(2)	-32(4)
O(2)	78(4)	198(9)	69(3)	17(4)	35(3)	-5(4)
O(3)	45(4)	71(4)	76(3)	8(2)	17(2)	8(3)
O(4)	74(3)	140(7)	111(4)	21(4)	42(3)	66(4)
O(5)	87(3)	178(8)	40(2)	43(4)	3(2)	2(3)
O(6)	82(4)	138(7)	137(5)	9(4)	-66(4)	-48(5)
O(7)	38(2)	108(5)	71(3)	5(2)	0(2)	-14(3)
O(8)	34(2)	115(5)	67(3)	-3(2)	3(2)	-27(3)
O(9)	53(2)	169(7)	88(3)	-27(3)	-4(2)	-51(4)
O(10)	43(2)	127(6)	65(3)	-12(3)	7(2)	-17(3)
O(11)	44(2)	149(6)	58(3)	-16(3)	4(2)	-10(3)
O(12)	80(3)	195(8)	88(4)	-39(4)	42(3)	-67(4)
O(13)	47(2)	145(7)	91(4)	11(3)	12(2)	27(4)
O(14)	40(2)	110(5)	88(3)	-11(3)	1(2)	-1(3)
O(15)	146(6)	72(5)	123(5)	-19(4)	40(4)	-10(4)
O(16)	48(2)	134(6)	70(3)	-5(3)	1(2)	15(3)
O(17)	44(2)	135(6)	56(2)	-5(3)	4(2)	8(3)
O(18)	94(4)	189(8)	66(3)	-9(4)	22(3)	24(4)
O(19)	52(3)	132(7)	107(4)	1(3)	2(3)	14(4)
O(20)	45(2)	189(8)	82(3)	18(3)	-12(2)	1(4)
O(21)	53(3)	283(12)	157(6)	56(5)	-18(3)	6(7)
O(22)	38(2)	88(5)	69(3)	-7(2)	1(2)	4(3)
O(23)	38(2)	103(5)	74(3)	-3(2)	-8(2)	-9(3)
O(24)	60(3)	81(5)	115(4)	12(3)	-5(3)	6(4)
O(w)	53(2)	94(5)	80(3)	-9(3)	15(2)	14(3)
N(1)	39(2)	76(5)	93(4)	5(3)	18(2)	14(4)
N(2)	38(3)	181(11)	212(10)	-16(4)	35(4)	70(8)
N(3)	39(2)	96(6)	57(3)	-12(3)	1(2)	-10(3)
N(4)	47(3)	103(6)	60(3)	-15(3)	17(2)	-11(3)
N(5)	66(3)	86(6)	55(3)	-12(3)	9(2)	1(3)
N(6)	53(3)	100(6)	52(3)	-16(3)	6(2)	5(3)
N(7)	45(3)	169(9)	80(4)	20(4)	0(3)	32(5)
N(8)	40(2)	79(5)	58(3)	6(3)	3(2)	5(3)
C(1)	43(3)	116(9)	125(7)	-18(4)	-8(4)	-12(6)
C(2)	42(3)	225(14)	116(7)	9(6)	-35(4)	-37(8)
C(3)	117(9)	576(39)	74(7)	-89(15)	1(6)	-117(13)
C(4)	147(10)	445(28)	53(5)	100(14)	-10(5)	-90(9)
C(5)	86(7)	378(27)	126(9)	64(11)	61(7)	30(13)
C(6)	50(4)	230(16)	242(15)	38(7)	74(7)	92(13)
C(7)	48(3)	105(8)	123(6)	4(4)	36(4)	0(6)
C(8)	50(3)	91(7)	83(5)	15(4)	24(3)	8(5)
C(9)	52(3)	68(6)	94(5)	2(4)	10(3)	23(4)
C(10)	83(5)	134(9)	81(5)	28(5)	13(4)	54(6)
C(11)	90(6)	252(17)	112(7)	-6(8)	45(5)	96(9)
C(12)	71(6)	333(23)	333(20)	33(9)	93(9)	232(19)
C(13)	69(4)	138(10)	118(7)	6(5)	52(5)	52(7)
C(14)	133(8)	155(11)	76(5)	44(7)	61(6)	48(8)
C(15)	242(14)	301(22)	47(4)	136(15)	-63(6)	-46(8)
C(16)	170(13)	369(31)	152(13)	61(16)	-74(10)	-144(17)
C(17)	151(12)	354(27)	172(13)	-175(16)	-108(10)	108(15)
C(18)	35(5)	379(32)	383(28)	-59(9)	-35(9)	-69(23)

^a The coefficients given are for the temperature factor $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$.

angle of 6.1° with the best plane through atoms O(2), O(4), O(6), and O(23), which make up the other. The best line through N(1), Sm(1), and N(2) is at an angle of about 86° to each of these planes. The Sm-N and Sm-O bond lengths (Table III) are in the normal range for these elements and agree with those found for other cryptates when ionic size and liganity number are taken into account.

The degree to which the ligand has been opened upon insertion of the NO_3^- ion is shown by examining the dihedral angle between pairs of best planes through the amine N atoms and the two other O atoms of each strand of the ligand. Between planes separated by the NO_3^- ion the angle is 159°, and between each of the other pairs it is about 90°.

The mean values of bond lengths and angles in the [2.2.2] molecule are similar to those found in other determinations, e.g., that of $Ca[2.2.2]Br_2 \cdot 3H_2O$.^{2f} The values for the present compound are C-C = 1.45, O-C = 1.43, and N-C = 1.48 Å and O-C-C = 110, N-C-C = 113, C-O-C = 115, and C-N-C = 109°. There is, however, considerable distortion from the conformation of the free ligand, even more than for Na^+ or Ca^{2+} complexes whose radii are close to Sm^{3+} . This is clearly evidenced in a comparison of the torsion angles given in Table IV.

The complex anion in this structure, $[Sm(NO_3)_5 \cdot H_2O]^{2-}$, has all its NO_3^- ions attached in bidentate fashion. For each of these, as well as the NO_3^- ion in the cation, the N-O bonds in the side toward the Sm^{3+} ion are longer by about 0.04 Å than those on the free sides. From interatomic distances throughout the structure it appears that the H_2O molecule,

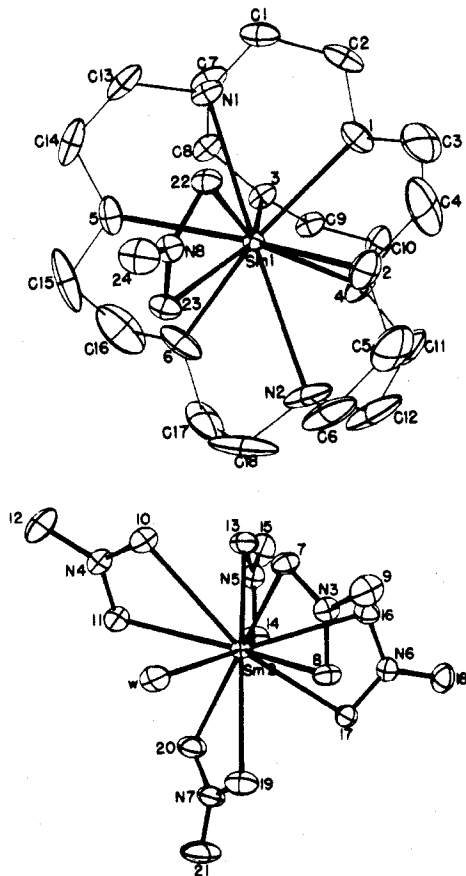


Figure 1. View of the cation and anion, indicating the numbering of atoms and showing their thermal ellipsoids (20% probability). Oxygen atoms are labeled only by numbers: (top) cation $(C_{18}H_{36}O_6N_2SmNO_3)^{2+}$; (bottom) anion $[Sm(NO_3)_5 \cdot H_2O]^{2-}$.

which is part of the large anion, acts as a donor of H atoms, forming weak hydrogen bonds to other anions. Recipient atoms are O(12) and O(15) belonging to nitrate ions in different large anions. Their distances from O(w) are 2.87 and 2.95 Å, respectively. The O(12)-O(w)-O(15) angle is 100.5°. The closest nonbonded approach between atoms of different large ions is 3.14 Å between C(2) and C(13); all other interionic contacts are greater than 3.4 Å.

In each of the lanthanide cryptates whose structures are now known, La[2.2.2]⁶, Sm[2.2.2], and Eu[2.2.2],⁷ the central lanthanide ion has, in addition to the cryptand surrounding it, one or two bidentate ions attached to it and situated between

Table III. Interatomic Distances and Standard Deviations (Å)

Sm(1)-N(1)	2.748 (5)	N(6)-O(16)	1.262 (7)
N(2)	2.779 (6)	O(17)	1.247 (6)
O(1)	2.496 (4)	O(18)	1.227 (6)
O(2)	2.566 (5)	N(7)-O(19)	1.254 (8)
O(3)	2.441 (4)	O(20)	1.260 (7)
O(4)	2.473 (4)	O(21)	1.197 (7)
O(5)	2.536 (4)	N(8)-O(22)	1.263 (6)
O(6)	2.470 (5)	O(23)	1.271 (6)
O(22)	2.502 (4)	O(24)	1.194 (6)
O(23)	2.484 (4)		
N(1)-C(1)	1.475 (9)	C(1)-C(2)	1.48 (1)
C(7)	1.507 (7)	C(2)-O(1)	1.47 (1)
C(13)	1.488 (8)	O(1)-C(3)	1.37 (1)
N(2)-C(6)	1.52 (1)	C(3)-C(4)	1.34 (2)
C(12)	1.46 (1)	C(4)-O(2)	1.40 (1)
C(18)	1.44 (2)	O(2)-C(5)	1.39 (1)
N(1)	5.53 (1)	C(5)-C(6)	1.50 (2)
N(3)-O(7)	1.258 (6)	C(7)-C(8)	1.50 (1)
O(8)	1.257 (6)	C(8)-O(3)	1.47 (1)
O(9)	1.222 (6)	O(3)-C(9)	1.44 (1)
N(4)-O(10)	1.256 (6)	C(9)-C(10)	1.47 (1)
O(11)	1.259 (6)	C(10)-O(4)	1.44 (1)
O(12)	1.233 (6)	O(4)-C(11)	1.42 (1)
Sm(2)-O(7)	2.520 (4)	C(11)-C(12)	1.42 (2)
O(8)	2.506 (4)	C(13)-C(14)	1.50 (1)
O(10)	2.668 (4)	C(14)-O(5)	1.44 (1)
O(11)	2.509 (4)	O(5)-C(15)	1.50 (1)
O(13)	2.585 (4)	C(15)-C(16)	1.49 (2)
O(14)	2.547 (4)	C(16)-O(6)	1.31 (1)
O(16)	2.556 (4)	O(6)-C(17)	1.45 (1)
O(17)	2.535 (4)	C(17)-C(18)	1.34 (2)
O(19)	2.614 (5)	O(w)-O(10)	2.835 (6)
O(20)	2.493 (5)	O(w)-O(12)	2.871 (7)
O(w)	2.493 (4)	O(w)-O(19)	2.785 (7)
N(5)-O(13)	1.267 (7)		
O(14)	1.253 (7)		
O(15)	1.222 (6)		

the ligand strands. This is attributable to the fact that lanthanide ions involved usually have a coordination number higher by 1-3 than that provided by just the ligand and because these ions are too small (radius 0.95-1.06 Å) to fill the intermolecular cavity of [2.2.2], which Mathieu et al.² have concluded is 1.4-1.5 Å. Thus the flexibility of the cryptand and the strong attraction by the trivalent lanthanide result in all the heteroatoms of the [2.2.2] being included in the coordination and the ligand strands being separated to allow the close approach of the small ion(s). The resulting coordination number is 10 for the cryptates of Sm and Eu and 12 for La. The stability of these three cryptates in solution has not been

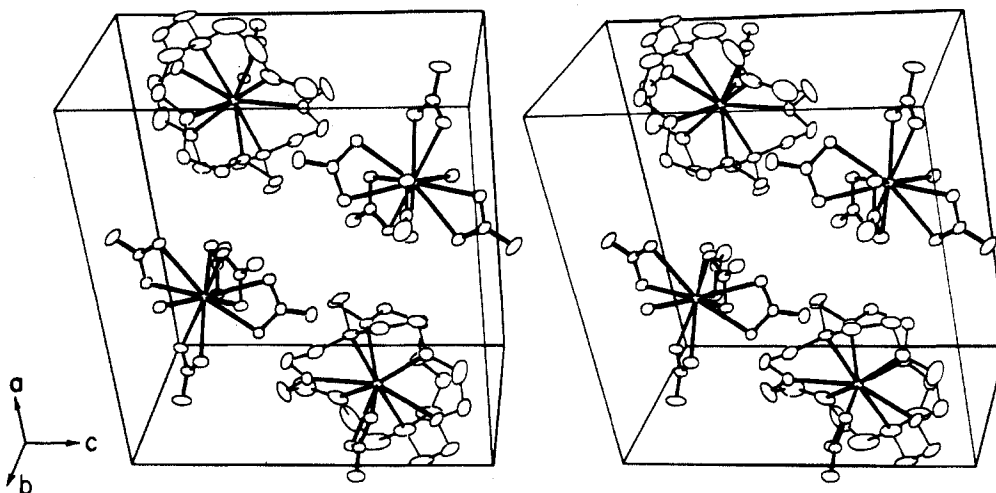


Figure 2. Stereoscopic view of one triclinic unit cell to show the packing of cations and anions.

Table IV. Torsion Angles^a (deg) of the [2.2.2] Ligand When Alone and When Enclosing Various Ions

A-B-C-D ^b	pure [2.2.2]	Na- [2.2.2]	Ca- [2.2.2]	Sm- [2.2.2]
N(1)-C(1)-C(2)-O(1)	-69	-41	-57	-60
C(1)-C(2)-O(1)-C(3)	167	148	-178	-119
C(2)-O(1)-C(3)-C(4)	-180	-162	-97	156
O(1)-C(3)-C(4)-O(2)	-175	45	-59	14
C(3)-C(4)-O(2)-C(5)	175	-153	-96	157
C(4)-O(2)-C(5)-C(6)	94	163	-178	-180
O(2)-C(5)-C(6)-N(2)	-68	-58	-57	42
N(1)-C(7)-C(8)-O(3)	-76	c	-58	-48
C(7)-C(8)-O(3)-C(9)	90		-161	-130
C(8)-O(3)-C(9)-C(10)	174		-82	155
O(3)-C(9)-C(10)-O(4)	-178		-53	49
C(9)-C(10)-O(4)-C(11)	-172		-155	142
C(10)-O(4)-C(11)-C(12)	173		177	-148
O(4)-C(11)-C(12)-N(2)	-69		-34	-35
N(1)-C(13)-C(14)-O(5)	-67	c	-33	47
C(13)-C(14)-O(5)-C(15)	109		172	176
C(14)-O(5)-C(15)-C(16)	178		-149	144
O(5)-C(15)-C(16)-O(6)	179		-52	46
C(15)-C(16)-O(6)-C(17)	-176		-78	135
C(16)-O(6)-C(17)-C(18)	155		-164	-151
O(6)-C(17)-C(18)-N(2)	-68		-59	-47

^a Defined as the angle,¹⁴ measured counterclockwise, that the projection of bond A-B makes relative to the bond C-D when viewed along the direction B-C. Estimated standard deviations are about 1°. ^b A renumbering of atoms from other papers has been made in order to compare with the present work. Of necessity this is somewhat arbitrary because there is no way to distinguish between the N atoms or among the different strands of the ligands. ^c All three strands are identical because of threefold symmetry.

measured, but it is probably small in view of the strains induced by formation of these molecule ions.

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Registry No. $(\text{C}_{18}\text{H}_{36}\text{O}_6\text{N}_2)\text{Sm}_2(\text{NO}_3)_6\cdot\text{H}_2\text{O}$, 71425-97-3.

Supplementary Material Available: A listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Preparation and Structural Characterization of the Mono- and Bis(triphenylphosphine)-Substituted Derivatives of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$. Effect of Phosphine Ligand Substitution on the Co_2As_2 Metal Cluster System¹

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The tricyclic dinuclear $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ complex and its mono- and bis(triphenylphosphine)-substituted derivatives have been prepared and characterized. Single-crystal X-ray diffraction analyses of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ and $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ have confirmed the postulated $\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2)$ -type geometry for the Co_2As_2 core and have revealed short As-As bond lengths of 2.273 (3) and 2.281 (3) Å, respectively, which is interpreted as an indication of significant As_2 multiple-bond character. A comparison of the molecular parameters for both of these derivatives of $\text{Co}_2(\text{CO})_6(\mu\text{-As}_2)$ demonstrates that the tricyclic Co_2As_2 core remains largely unperturbed by the replacement of an axial carbonyl ligand with a triphenylphosphine ligand. Crystals of $\text{Co}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3](\mu\text{-As}_2)$ are triclinic, space group $P\bar{1}$, with $a = 11.391$ (8) Å, $b = 13.033$ (9) Å, $c = 9.120$ (7) Å, $\alpha = 108.17$ (1)°, $\beta = 103.84$ (1)°, and $\gamma = 74.22$ (1)°; $\rho_{\text{obsd}} = 1.82$ g/cm³ vs. $\rho_{\text{calcd}} = 1.80$ g/cm³ for $Z = 2$. Least-squares refinement gave $R_1(F) = 7.3\%$ and $R_2(F) = 7.4\%$ for 1911 independent reflections with $I > 2\sigma(I)$. Crystals of $\text{Co}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\mu\text{-As}_2)$ are monoclinic, space group C2, with $a = 12.685$ (5) Å, $b = 14.660$ (6) Å, $c = 10.107$ (4) Å, and $\beta = 97.73$ (1)°; $\rho_{\text{obsd}} = 1.59$ g/cm³ vs. $\rho_{\text{calcd}} = 1.61$ g/cm³ for $Z = 2$. Least-squares refinement gave $R_1(F) = 4.7\%$ and $R_2(F) = 5.3\%$ for 1093 independent observed reflections with $I > 2\sigma(I)$.

Introduction

$\text{Co}_2(\text{CO})_6\text{As}_2$ is a member of the homologous series $\text{As}_{4-n}[\text{Co}(\text{CO})_3]_n$ ($n = 0-4$) in which the arsenic atoms of the tetrahedral As_4 molecule are successively replaced by electronically equivalent $\text{Co}(\text{CO})_3$ moieties. The $\text{Co}_2(\text{CO})_6\text{As}_2$

complex was prepared from the reaction of $\text{Co}_2(\text{CO})_8$ with AsCl_3 .⁵ The molecular formula of this red, air-sensitive liquid (mp -10 °C) was determined from mass spectral analysis, and its diamagnetism was established by the NMR method. On the basis of the close similarity of the infrared spectrum of