TABLE V

INTERMOLECULAR DISTANCES IN CYANIDE COMPOUNDS

Distance	Compd	Value, A	van der Waals distance,[a] A	Ref
Ge–N	$(CH_3)_3GeCN$	3.57	3.5	*b*
As–N	$As(CN)_3$	2.74	3.5	*c, d*
As–N	$CH_3As(CN)_2$	2.94	3.5	*d*
As–N	$(CH_3)_2AsCN$	3.18	3.5	*e*
Se–N	$Se(CN)_2$	2.6	3.5	*f*
Br–N	BrCN	2.9	3.45	*g*

[a] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260. [b] This work. [c] K. Emerson and D. Britton, *Acta Cryst.*, 16, 113 (1963). [d] E. O. Schlemper and D. Britton, *ibid.*, in press. [e] N. Camerman and J. Trotter, *Can. J. Chem.*, **41**, 460 (1963). [f] A. C. Hazell, *Acta Cryst.*, 16, 843 (1963). The value given in this table is based on C–N = 1.16 rather than the 1.42 reported; Hazell gives Se–N = 2.35. [g] S. Geller and A. L. Schawlow, *J. Chem. Phys.*, **23**, 779 (1955).

point toward the next central atom.[8] In the latter compounds the packing is determined by the approximate cubic close packing of the iodide atoms. In the trimethylcyanogermane structure, the packing can be regarded as approximate hexagonal close packing of the methyl and cyano groups, and this alone may be the significance of the molecular arrangement.

In summary, the packing and the distances in crystalline $(CH_3)_3GeCN$ do not rule out the possibility of an interaction between the adjacent nitrogen and germanium atoms, but they also do not demonstrate one. It is only a pleasant speculation to imagine that the arrangement in the crystal is the first step toward the more striking arrangement of planar $(CH_3)_3Sn$ groups and equally shared CN groups found in $(CH_3)_3SnCN$.[4]

Acknowledgments.—We thank the National Aeronautical and Space Agency for a fellowship for E. O. S. and the National Science Foundation for their support of this work. The necessary germanium tetrachloride was generously provided by the Germanium Information Center. We thank Professor Robert Jacobson, Mr. Byron Gorres, and Mr. L. W. Finger for providing us with copies of their computer programs and for helping us with their use. We thank Mrs. Judith Konnert for help with many of the computations.

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[8] R. W. G. Wyckoff, "Crystal Structures," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 5.

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
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Structure of $K_2BaCo(NO_2)_6$

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Received August 18, 1965

The structure of $K_2BaCo(NO_2)_6$ has been determined from three-dimensional data. The substance crystallizes as cubic crystals of space group Fm3 with a = 10.66 A. The cobalt occupies a site of S_6 symmetry; the nitrite ion is not significantly distorted from its structure in sodium nitrite.

Introduction

As part of a study of low-spin d^7 complexes, we became interested in the structure of the complex $Co(NO_2)_6{}^{4-}$. Although low-spin octahedral complexes of d^7 ions are expected to be distorted by a Jahn–Teller effect, various compounds of the formula $M_2M'Co(NO_2)_6$ (where M represents a univalent and M′ a divalent cation) are cubic,[2] according to powder patterns. It is also of interest that corresponding copper(II) compounds show identical powder patterns,[2] and single-crystal X-ray studies have been carried out on $K_2PbCu(NO_2)_6$,[3,4] using two-dimensional data. There is some disagreement, however, as to the space group, and the results of the two studies are somewhat different; the differences are limited to the oxygen positions since the other atoms occupy the same special positions in either of the two space groups, Fm3 or F23.

Because of the disagreement over space group and because both studies show the nitrite ion considerably distorted from its structure in sodium nitrite,[5] we have collected three-dimensional X-ray diffraction data for a crystal of $K_2BaCo(NO_2)_6$ and have redetermined the structure.

Collection and Reduction of the X-Ray Data

Previous studies employed $K_2PbCu(NO_2)_6$ because it readily forms large crystals, while most other copper and cobalt compounds of the same type give only microcrystalline products which are unsuitable for single crystal studies. By employing slow mixing and using acetate as anion for both the cobalt and barium ions, it was possible to grow crystals of $K_2BaCo(NO_2)_6$ *ca.* 0.1 mm at their widest point; the crystals were octahedral in shape.

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[1] U. S. Steel Fellow, Georgia Institute of Technology, 1965.

[2] A. Ferrari, L. Cavalca, and M. Nardelli, *Gazz. Chim. Ital.*, **81**, 982 (1951); A. Ferrari and C. Cola, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, [6] **14**, 435 (1931); [6] **11**, 755 (1930).

[3] M. van Driel and H. J. Verwell, *Z. Krist.*, **95**, 308 (1936).

[4] L. Cavalca, M. Nardelli, and D. Grazioli, *Gazz. Chim. Ital.*, **86**, 1041 (1956).

[5] M. I. Kay and R. C. Fraser, *Acta Cryst.*, **14**, 56 (1961).

Data were collected with a precession camera, using Mo Kα radiation; the unit cell parameter a was 10.66 ± 0.03 A. To consider the possibility that the crystals were only pseudo-cubic, *i.e.*, a cubic arrangement of the heavy atoms but lower symmetry for the nitrite positions, we initially collected two zero-level zones, $hk0$ and $0kl$; comparison of reflections related by the threefold axis of cubic symmetry showed no differences greater than reading errors. Additional zones, xkl (x = 1–3), were collected. The diffraction photographs showed systematic extinctions for $(h + k)$, $(k + l)$, and $(h + l)$ odd, and the photographs exhibited mm symmetry, consistent with space groups Fm3 and F23.

In addition, odd levels (h = 1, 3) exhibited apparent fourfold symmetry. Since, according to previous workers and consistent with our findings, all atoms except oxygen occupy the same special positions in either space group and since all atoms except oxygen occupy positions of fourfold symmetry, the possibility of the oxygens contributing only to even levels was suggested. A comparison of the form of the structure factor calculations for the two space groups shows that in Fm3 the oxygen coordinates occur only in factors such as cos $(2\pi hx)$, and the oxygen contribution would thus be zero if one coordinate were equal to $^1/_4$; since oxygen coordinates occur in factors such as sin $(2\pi hx)$ as well as factors such as cos $(2\pi hx)$ in F23, there is no apparent reason for the oxygens *not* contributing to all levels in F23. As one of the oxygen coordinates was $^1/_4$ in previous studies, Fm3 appears to be the correct space group, and this choice is verified by the structure refinement. We have also mounted a crystal of $K_2PbCu(NO_2)_6$ and observed the same effect.

Intensities were estimated visually for 118 independent reflections and Lorentz-polarization corrections were computed;[6] no corrections were made for absorption.

Solution and Refinement of the Structure

With four molecules per unit cell[2] and only two sets of fourfold special positions, the 4a positions were used for the cobalt atoms and the 4b positions were used for the barium atoms; the potassium atoms were placed on the one eightfold set, 8c. After one cycle of least-squares refinement of layer scale factors and individual atom temperature factors, a structure factor calculation with the metal atoms in these special positions, with fixed coordinates as indicated in Table I, gave a conventional R value of 0.25; a difference Fourier, with signs from the heavy atom contribution, located the nitrogen and oxygen positions. With all observed reflections weighted at unity and unobserved reflections omitted, least-squares refinements of the one variable coordinate of nitrogen, two variable coordinates of oxygen, layer scale factors, and independent atom temperature factors were continued until successive cycles gave no appreciable change in any parameter; the final R value was 0.07. Table I lists the final structure parameters; Table II lists observed and calculated structure factors. To express the F_o values in electrons, the values in Table II must be multiplied by scale factors; the scale factors for the $0kl$, $1kl$, $2kl$, and $3kl$ reflections are 20.46, 22.92, 21.60, and 24.73, respectively.

TABLE I

STRUCTURE PARAMETERS FOR $K_2BaCo(NO_2)_6$

Atom	x	y	z	B, A^2
Ba	0.500[a]	0.500	0.500	2.3(1)
K	0.250	0.250	0.250	4.3(3)
Co	0.000	0.000	0.000	0.2(2)
Ni	0.186(2)	0.000	0.000	2.6(5)
O	0.000	0.249(2)	0.096(1)	3.3(3)

[a] Parameters not followed by parentheses are symmetry fixed; numbers in parentheses here and in Table III are estimated standard deviations in the least significant digits.

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES FOR $K_2BaCo(NO_2)_6$

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	6	0	62	71	0	8	10	30	29	2	12	0	33	34	2	12	10	23	20
0	10	0	61	62	0	10	10	37	31	2	6	2	54	55	2	14	10	11	10
0	14	0	24	23	0	0	12	66	66	2	10	2	18	20	2	2	12	33	34
0	0	2	142	131	0	4	12	54	47	2	14	2	20	16	2	4	12	29	31
0	2	2	148	137	0	6	12	35	27	2	2	4	158	145	2	6	12	34	34
0	4	2	19	24	0	8	12	40	33	2	4	4	57	61	2	8	12	17	19
0	8	2	38	38	0	2	14	29	28	2	6	4	130	129	2	10	12	20	17
0	12	2	30	31	1	3	1	48	46	2	8	4	22	28	2	12	12	14	12
0	0	4	254	252	1	5	1	13	14	2	10	4	46	53	3	5	1	27	25
0	2	4	158	153	1	7	1	24	25	2	12	4	15	20	3	9	1	22	22
0	4	4	122	130	1	9	1	17	18	2	14	4	32	27	3	13	1	14	11
0	6	4	75	88	1	3	3	59	59	2	0	6	70	73	3	3	3	62	62
0	8	4	71	83	1	5	3	28	29	2	4	6	82	86	3	5	3	30	35
0	10	4	57	64	1	9	3	24	20	2	6	6	66	68	3	7	3	35	34
0	12	4	36	47	1	13	3	14	13	2	8	6	42	44	3	11	3	13	16
0	14	4	29	24	1	5	5	9	11	2	10	6	31	29	3	5	5	16	1[illegible]
0	4	6	20	20	1	7	5	14	16	2	12	6	24	25	3	7	5	21	20
0	6	6	79	86	1	9	5	13	14	2	14	6	20	18	3	9	5	14	17
0	8	6	31	28	1	3	7	33	32	2	2	8	62	64	3	1	7	30	29
0	10	6	65	61	1	5	7	16	18	2	4	8	48	48	3	5	7	22	21
0	12	6	30	24	1	7	7	23	19	2	6	8	62	65	3	7	7	24	21
0	0	8	122	133	1	9	7	15	15	2	8	8	25	25	3	9	7	15	1[illegible]
0	2	8	64	64	1	5	9	12	13	2	10	8	29	30	3	3	9	27	26
0	4	8	80	83	1	7	9	13	15	2	12	8	17	16	3	5	9	15	16
0	6	8	44	44	1	9	9	11	12	2	14	8	16	16	3	7	9	16	17
0	8	8	57	57	1	1	11	11	9	2	0	10	66	60	3	9	9	15	13
0	10	8	46	37	1	3	11	13	13	2	4	10	63	61	3	1	11	12	12
0	12	8	45	33	1	1	13	14	10	2	6	10	28	29	3	3	13	14	13
0	4	10	39	37	2	6	0	125	129	2	8	10	39	35					
0	6	10	44	38	2	10	0	47	50	2	10	10	12	14					

Discussion of Structure

Table III compares interatomic distances and the O–N–O angle determined in this study with the results of earlier studies;[3,4] the N–O bond length and the O–N–O angle from this study are very similar to the values found for the nitrite ion in sodium nitrite[5] (1.24 A and 115°). Such similarity was expected since coordination does not usually cause appreciable distortion in the ligand, even when π-bonding effects are extreme (as in carbonyl complexes).

TABLE III

COMPARISON OF INTERATOMIC DISTANCES (A) AND O–N–O ANGLE OF THIS STUDY WITH EARLIER STUDIES

		$K_2PbCu(NO_2)_6$	
Atoms	$K_2BaCo(NO_2)_6$	Ref 3	Ref 4
Co–N (or Cu–N)	1.98 (2)	2.24	2.03
N–O	1.23 (2)	1.15	1.38
Ba–O (or Pb–O)	2.87 (2)	2.87	2.72
K–O	3.13 (1)	3.10	3.13
O–N–O angle	114° (2°)	136°	108°

The difference between the barium–oxygen distance of 2.87 A in this structure and the sodium–oxygen

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(6) All computations were made on the Burroughs B-5500 computer. Programs for Lorentz-polarization corrections and Fourier summations were written by J. A. B.; translations of the Busing, Levy, and Martin ORFLS least-squares refinement and ORFFE function and error programs were used.

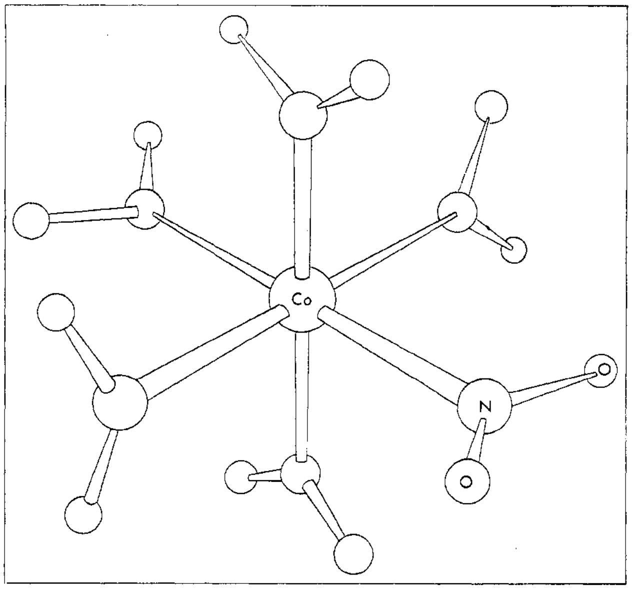

Figure 1.—A perspective drawing of $Co(NO_2)_6^{4-}$. The cobalt and the atoms of one nitrite ion are labeled.

distance of 2.47 A in sodium nitrite is the same as the difference in ionic radii between barium and sodium. Although the structure is, therefore, well described as made up of discrete ions, the change in color of the compounds with change in M′ (becoming darker in color down the periodic table in the alkaline earth series, much darker for Pb^{2+}) indicates that there is at least some charge-transfer interaction between the complex and the divalent metal ion, M′.

In the hexanitrocobaltate(II) ion, Figure 1, the nitrites are monodentate and coordinated through the nitrogen. Although the structure shows six nitrogen atoms octahedrally surrounding the cobalt(II), the actual crystallographic site symmetry of the cobalt(II) is lower than octahedral. The lower symmetry would be of no consequence if a point-charge model were used to discuss the complex; however, any attempt to consider π bonding would involve the nitrogen π orbitals, and the effective symmetry would be S_6.

Since π-bonding effects are probably appreciable in this complex, the lower symmetry may account for the lack of distortion in the cobalt and copper compounds; although an electronic degeneracy remains in both d^7 and d^9 cases in S_6 symmetry, the orbitals do not point directly at the ligands. The orientation of the orbitals with respect to ligands would be similar to the orientation of the T_{2g} orbitals in O_h symmetry, and degeneracies of the T_{2g} orbitals are expected to produce smaller distortions than degeneracies of the E_g orbitals in octahedral symmetry.

Another alternative to explain the lack of distortion would be a dynamic Jahn–Teller effect; however, temperature-dependent magnetic studies[7] showed no unusual featues down to 80°K. Thus, if there is a dynamic effect, it does not appear possible to freeze this into a static effect above 80°K.

Acknowledgment.—This work was supported in part by the National Aeronautics and Space Administration under Grant NsG-657. The help of the Rich Electronic Computer Center of Georgia Institute of Technology with computations is gratefully acknowledged. Translations from Fortran to Extended Algol of the ORFLS program by L. J. Gallaher and M. I. Kay and of the ORFFE program by L. J. Gallaher and F. C. Taylor, Jr., are also gratefully acknowledged.

[7] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

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The Molecular and Crystal Structure of Bis(1-phenyl-1,3-butanedionato)copper[1]

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Received July 8, 1965

The structure of the *trans* form of bis(benzoylacetonato)copper(II) has been determined from three-dimensional X-ray diffraction data. The crystals are monoclinic, space group $P2_1/c$ with $a = 4.475$ A, $b = 10.640$ A, $c = 18.486$ A; $\beta = 97° 40'$, $Z = 2$. The crystal is made up of discrete monomers. In each molecule the four oxygens and the copper atom are exactly coplanar. The copper–oxygen distances are 1.94 and 1.91 A. The carbon–oxygen distances are 1.24 and 1.29 A. The carbon–carbon distances agree with the usual acceptable values. The standard deviation is 0.005 A for Cu–O bonds and 0.010 A for C–O and C–C bonds.

Introduction

A structure determination of vanadyl bisbenzoylacetonate[2] showed differences among the V–O bond lengths. The variation was attributed to inductive and resonant effects of the phenyl group. For a comparison, and for analysis of a proposed crystal spectroscopic study, we undertook the determination of the crystal

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[1] This research was aided by U. S. Public Health Services Grant GM-10907, under the auspices of the Division of General Medical Sciences, and by the University of Illinois Graduate Research Board.

[2] P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**, 1323 (1965).