Table III. Interatomic Distances (Å) and Angles (Deg) for $[Mo(CNPh)_7](PF_6)_2$[a]

	Coordination Sphere[b]		
Mo-C(71)	2.059(11)	Mo-C(41)	2.152(11)
Mo-C(51)	2.094(9)	Mo-C(31)	2.156(9)
Mo-C(11)	2.105(10)	Mo-C(61)	2.191(10)
Mo-C(21)	2.107(10)		
C(21)-Mo-C(41)	169.5(4)	C(31)-Mo-C(61)	86.0(3)
C(11)-Mo-C(31)	159.2(4)	C(21)-Mo-C(31)	84.4(4)
C(51)-Mo-C(61)	156.2(4)	C(21)-Mo-C(61)	82.1(4)
C(61)-Mo-C(71)	131.9(4)	C(41)-Mo-C(51)	77.1(4)
C(31)-Mo-C(71)	127.9(4)	C(11)-Mo-C(61)	76.7(4)
C(41)-Mo-C(71)	118.7(4)	C(31)-Mo-C(51)	76.7(3)
C(11)-Mo-C(51)	115.9(4)	C(11)-Mo-C(41)	75.5(4)
C(21)-Mo-C(51)	111.8(4)	C(11)-Mo-C(71)	72.8(4)
C(11)-Mo-C(21)	104.2(4)	C(51)-Mo-C(71)	71.9(4)
C(31)-Mo-C(41)	92.5(4)	C(21)-Mo-C(71)	70.6(4)
C(41)-Mo-C(61)	87.6(4)		
	Ligand Geometry[c]		
C(11)-N(11)	1.133(12)	N(11)-C(12)	1.355(11)
C(21)-N(21)	1.152(14)	N(21)-C(22)	1.378(12)
C(31)-N(31)	1.153(12)	N(31)-C(32)	1.367(10)
C(41)-N(41)	1.134(14)	N(41)-C(42)	1.378(11)
C(51)-N(51)	1.146(12)	N(51)-C(52)	1.376(10)
C(61)-N(61)	1.129(12)	N(61)-C(62)	1.363(10)
C(71)-N(71)	1.142(14)	N(71)-C(72)	1.376(12)
Mo-C(11)-N(11)	177.0(9)	C(11)-N(11)-C(12)	176.4(11)
Mo-C(21)-N(21)	173.2(8)	C(21)-N(21)-C(22)	173.3(8)
Mo-C(31)-N(31)	177.1(9)	C(31)-N(31)-C(32)	175.3(10)
Mo-C(41)-N(41)	172.0(8)	C(41)-N(41)-C(42)	174.9(9)
Mo-C(51)-N(51)	178.9(9)	C(51)-N(51)-C(52)	174.9(9)
Mo-C(61)-N(61)	177.5(8)	C(61)-N(61)-C(62)	178.2(10)
Mo-C(71)-N(71)	176.3(9)	C(71)-N(71)-C(72)	171.8(10)
	Anion Geometry		
min P-F	1.526(9)	mean cis F-P-F	90.0(5)
max P-F	1.601(7)	min trans F-P-F	178.1(6)
mean P-F	1.566(8)	max trans F-P-F	179.5(4)
min cis F-P-F	87.6(6)	mean trans F-P-F	178.8(5)
max cis F-P-F	93.1(6)		

[a] See footnote *a*, Table II. Distances have not been corrected for thermal motion. Standard deviations, quoted for mean values, are the average of the standard deviation for the individual values. [b] Distances and angles at the metal are listed in increasing and decreasing size, respectively. [c] Phenyl rings were refined as rigid groups; see text.

1 shows the geometry of the cation along with the atom labeling scheme.

Discussion

The structure consists of discrete $[Mo(CNPh)_7]^{2+}$ cations and PF_6^- anions having no crystallographically imposed symmetry. The geometry of the anions is normal. The cations are seven-coordinate, confirming the original assignment.[5a] Their geometry approximates that of the 4:3 (C_s) piano stool structure recently identified in several related alkyl isocyanide Mo(II) and W(II) complexes.[3,4] This choice of geometry is made by comparing the C–Mo–C interbond angles of Table III with those tabulated[3g] for various reference geometries. In this description the quadrilateral face is defined by atoms C(11), C(41), C(51), and C(71) and the trigonal face by atoms C(21), C(31), and C(61) (Figure 1). After the bond lengths were normalized, the dihedral angle between the quadrilateral and trigonal faces was computed to be 1.04° while that across the diagonal of the quadrilateral face was found to be 2.58°. These values confirm the 4:3 (C_s) piano stool to be a good reference geometry.[3e,g] Alternatively, the structure may be referenced to an idealized C_{3v} capped octahedron with C(71) the capping (c) atom, C(11), C(21), and C(51) comprising the capped face (cf), and C(31), C(41), C(61) constituting the uncapped face (uf). With this latter reference geometry the familiar[4a,3h,3j] 1:3:3 bond length pattern emerges: Mo–C_c, 2.059 (11) Å; Mo–C_{cf}, 2.102 (average) Å; Mo–C_{uf}, 2.166 (average) Å. Similar results were found for the related seven-coordinate homoleptic cations $[Cr(CN\text{-}t\text{-}Bu)_7]^{2+}$[3j] and $[Mo(CNMe)_7]^{2+}$.[4a]

The mean Mo–C bond length of 2.123 ± 0.04 Å in the $[Mo(CNPh)_7]^{2+}$ cation is essentially the same as the corresponding mean distances in $[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}$ (2.115 ± 0.04 Å),[3b] $[Mo(CNMe)_7]^{2+}$ (2.107 ± 0.04 Å),[4a] and $[Mo(CN\text{-}c\text{-}C_6H_{11})_7]^{2+}$ (2.106 ± 0.04 Å).[3h] The internal geometry of the phenyl isocyanide ligands is summarized in Table III.

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Registry No. $[Mo(CNPh)_7](PF_6)_2$, 78653-88-0.

Supplementary Material Available: Tables S1–S3 reporting respectively final observed and calculated structure factors, final thermal parameters for the nonhydrogen atoms, and fixed hydrogen atom positional and isotropic thermal parameters (20 pages). Ordering information is given on any current masthead page.

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^{61}Ni Hyperfine Interactions in Dichlorobis[*o*-phenylenebis(dimethylphosphine)]nickel(III) Perchlorate, $[Ni(phmp)_2Cl_2]ClO_4$

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There are only a few instances[1-7] of EPR studies of low-spin nickel complexes that also give information on the metal hyperfine interaction. There are still fewer systems[6,7] that provide ligand hyperfine interaction from all the bonded ligand nuclei, in addition to the metal hyperfine interaction due to ^{61}Ni, to enable us to obtain a complete picture of the unpaired electron distribution in the complex. Detailed EPR studies of Ni(III) in the ligand environment of group 5B donors have revealed a highly delocalized wave function for the unpaired electron.[6,8-10]

An earlier analysis[10] of ligand hyperfine interaction by a single-crystal EPR study of $[Ni(phmp)_2Cl_2]ClO_4$ [where phmp is *o*-phenylenebis(dimethylphosphine)] revealed delocalization amounting to 68% of the unpaired spin density on the ligand nuclei. The present investigation on the d^7 low-spin nickel(III) complex enriched with 85% nickel-61 isotope is an attempt to have a critical look at this estimate on the basis of the ^{61}Ni hyperfine coupling tensor.

Experimental Section

The complexes $[Ni(phmp)_2Cl_2]ClO_4$ and $[Co(phmp)_2Cl_2]ClO_4$ were prepared according to the procedure reported earlier.[11] The nickel(III) complex enriched with the magnetic isotope ^{61}Ni was made with 85% isotopically pure NiO. A 1:1 mixture of acetonitrile and absolute alcohol was used for solution EPR measurements.

Single-crystal EPR measurements were made on $[^{61}Ni(phmp)_2Cl_2]^+$ magnetically diluted with the corresponding diamagnetic [Co-

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(1) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).
(2) R. D. Schmitt and A. H. Maki, *J. Am. Chem. Soc.*, **90**, 2288 (1968).
(3) R. K. Watts, *Phys. Rev.*, **188**, 568 (1969).
(4) U. Kaufmann, *Phys. Rev. B: Solid State*, **11**, 2478 (1975).
(5) W. E. Geiger, Jr., C. S. Allen, T. E. Mines, and F. C. Senftleber, *Inorg. Chem.*, **16**, 2003 (1977).
(6) F. C. Senftleber and W. E. Geiger, Jr., *Inorg. Chem.*, **17**, 3615 (1978).
(7) R. Kirmse, J. Stach, W. Dietzsch, G. Steimecke, and E. Hoyer, *Inorg. Chem.*, **19**, 2679 (1980).
(8) P. T. Manoharan and M. T. Rogers, *J. Chem. Phys.*, **53**, 1682 (1970).
(9) P. K. Bernstein and H. B. Gray, *Inorg. Chem.*, **11**, 3035 (1972).
(10) C. N. Sethulakshmi, S. Subramanian, M. A. Bennett, and P. T. Manoharan, *Inorg. Chem.*, **18**, 2520 (1979).
(11) L. F. Warren and M. A. Bennet, *Inorg. Chem.*, **15**, 3126 (1976).

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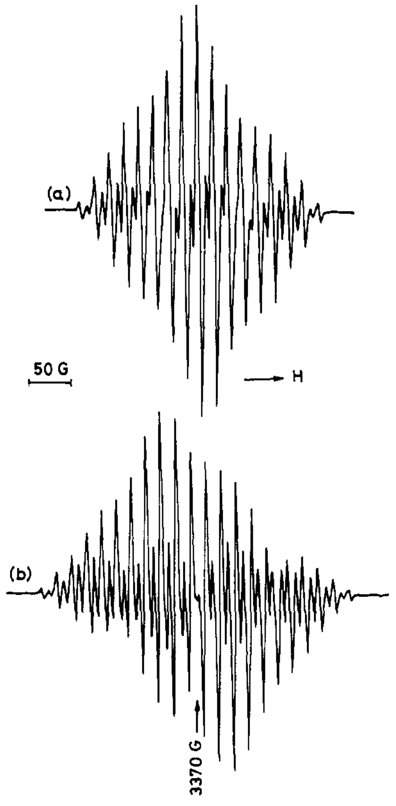

Figure 1. X-Band single-crystal EPR spectrum of (a) unenriched and (b) ^{61}Ni-enriched Ni^{III}/[Co(phmp)$_2$Cl$_2$]ClO$_4$. The magnetic field is parallel to the direction of the molecular z axis at T = 300 K.

(phmp)$_2$Cl$_2$]$^+$. The crystals were oriented in three orthogonal planes exactly as in the earlier work.[10] All the measurements were made at 300 K on a Varian E-4 X-band spectrometer with a 100-kHz modulation. DDPH was used as a g maker.

Results and Discussion

The magnetically diluted single crystals of [Ni(phmp)$_2$Cl$_2$]$^+$ contain 85% of the ^{61}Ni magnetic isotope and 15% of the nonmagnetic isotopes. The observed spectrum is the resultant of the overlap of spectra due to both species. Figure 1a,b represents the spectra due to the unenriched Ni(III) complex with the Ni isotopes in their natural abundance and the enriched complex, respectively, when the magnetic field is parallel to the z axis of the molecule. The ligand hyperfine lines due to phosphorus and chlorine are split into quartets by ^{61}Ni having a nuclear spin of $I = {}^3/_2$ and a magnetic moment of -0.7487 μ_N. The presence of additional EPR lines in the spectrum of the isotopically enriched complex is evident by comparing this with that of the complex containing nonmagnetic isotope for identical orientations. So the magnitude of the metal hyperfine splitting due to ^{61}Ni can be taken as one-third of the differences in the spectral spreads shown in Figure 1 for all the three orientations. The single-crystal spectra when the magnetic field is parallel to the g_{yy} direction in the molecule are shown in Figure 2. A slightly different spectrum was obtained along the g_{xx} direction. Any possibility of unequal spacings in the quartets due to ^{61}Ni, which would mainly arise from quadrupolar effects, has been neglected, due to its small quadrupole moment. It is also true that the analysis including quadrupole effects would almost be impracticable due to the high complexity of the spectra arising out of ligand interactions.

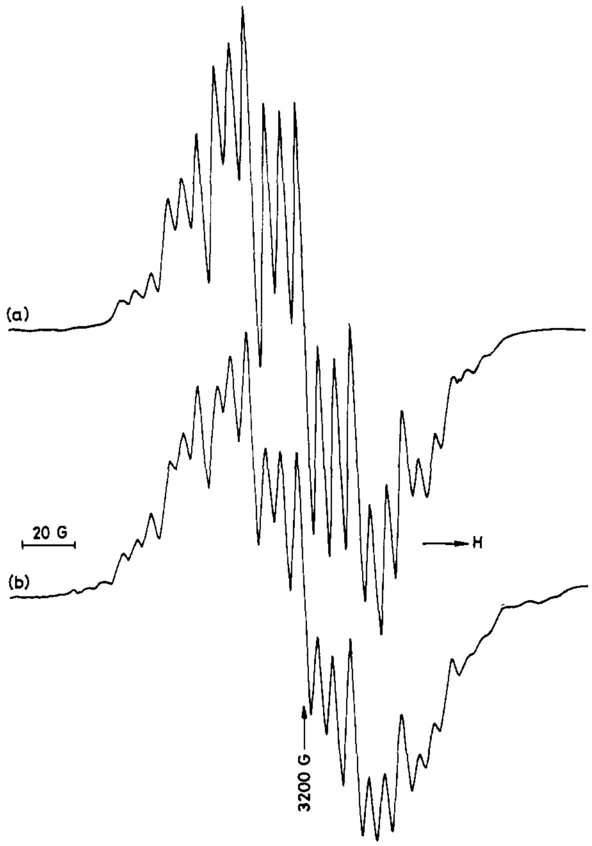

Figure 2. X-Band single-crystal EPR spectrum of (a) unenriched and (b) ^{61}Ni-enriched Ni^{III}/[Co(phmp)$_2$Cl$_2$]ClO$_4$. The magnetic field is parallel to the molecular y axis at T = 300 K.

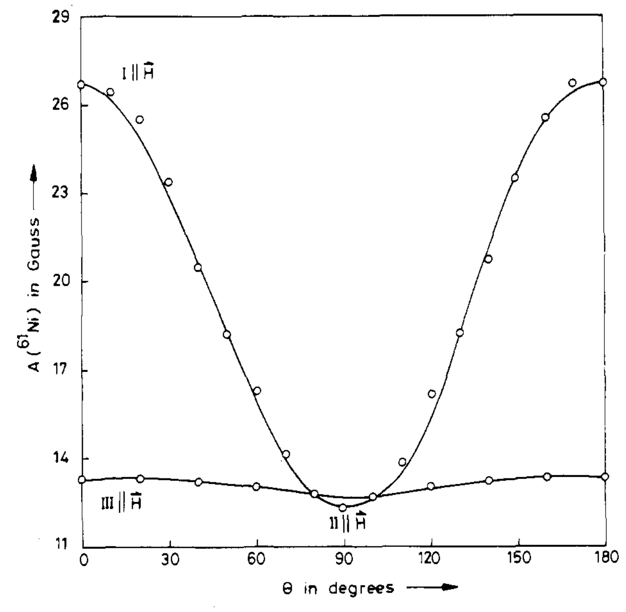

Figure 3. Angular variation of $A(^{61}\text{Ni})$, the metal hyperfine interaction due to ^{61}Ni isotope in the Ni^{III}/[Co(phmp)$_2$Cl$_2$]ClO$_4$ single crystal, for rotation about the crystal axes, I and III.

It may be noted that in the rotation about axis III (crystallographic b^*) the magnetic field is in the ac plane of the triclinic system. The other two axes are not identified with respect to the crystal framework. However, after diagonalization of the **g** tensor, it was confirmed that the direction cosines of the three axes coincide exactly with the three principal directions of the **g** tensor, viz., the molecular x, y, and z axes.

The angular variation study also reveals the coincidence of the **g** tensor and the **A** tensor due to ^{61}Ni. The angular variation of the ^{61}Ni hyperfine splitting tensor in the three orthogonal planes is shown in Figure 3.

The ^{61}Ni hyperfine tensor thus obtained is nearly axially symmetric: $A_{zz} = 25.0\ (\pm 0.5) \times 10^{-4}$ cm^{-1}, $A_{xx} = 13.1\ (\pm 0.4) \times 10^{-4}$ cm^{-1}, and $A_{yy} = 12.2\ (\pm 0.4) \times 10^{-4}$ cm^{-1}. Second-order perturbation expressions for the spin Hamiltonian parameters for the unpaired electron in a d_{z^2} orbital given by Maki et al.[1] are

$$g_{xx} = 2.0023 - 6b_1 \qquad g_{yy} = 2.0023 - 6b_2$$

$$g_{zz} = 2.0023 \qquad A_{xx} = P(-6b_1 - \kappa - {}^{2}\!/_{7} - {}^{3}\!/_{7}b_2)$$

$$A_{yy} = P(-6b_2 - \kappa - {}^{2}\!/_{7} - {}^{3}\!/_{7}b_1)$$

$$A_{zz} = P[-\kappa + {}^{4}\!/_{7} + {}^{3}\!/_{7}(b_1 + b_2)]$$

The coefficients b_1 and b_2 derived from the experimental g values ($g_{xx} = 2.1123$, $g_{yy} = 2.1157$, and $g_{zz} = 2.0089$) are used in deriving the Fermi contact term κ and the dipolar term P. Assuming A_{xx} and A_{yy} to be of the same sign (negative) and taking A_{zz} to be positive, we get $\kappa = 0.0816$ and $P = 52.7 \times 10^{-4}$ cm^{-1}. Substituting these, we derive $A_{yy} = 13 \times 10^{-4}$ cm^{-1}, which is in very good agreement with the experimental value. The relative signs thus obtained, viz., A_{zz} positive, A_{xx} and A_{yy} negative, are justified by the isotropic spectrum of the ^{61}Ni-enriched complex, which is identical with that reported for the unenriched (natural) Ni(III) complex.[10] The A_{av} obtained, with the assignment of these signs, viz., 0.1×10^{-4} cm^{-1}, is lower than the line width of the isotropic spectrum of the ^{61}Ni-enriched complex. The P value obtained corresponds to 42% (±2)% of the free-ion value[12] of 125.3×10^{-4} cm^{-1} calculated recently by Morton and Preston[12] with use of the Hermann–Skillman wave function for ^{61}Ni. Though this 58 (±2)% delocalization on the ligand is slightly lower than that predicted earlier[10] through spin-density calculations, in which 68 (±2)% of the unpaired electron density was found to be on the ligands, the results are in reasonably good agreement. The deviations may be explained as due to the neglect of other possible excited states contributing to the spin Hamiltonian parameters. It is significant to note that there is a marked deviation of g_{zz} (2.0089) from the free-electron g value predicted by second-order perturbation theory. Unfortunately this cannot be further quantified due to the simple experimental optical spectrum and very complex equations involving quartet and other doublet excited states. The noninclusion of ligand spin–orbit coupling due to the second-row ligands could have also been responsible.

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Registry No. $[Ni(phmp)_2Cl_2]ClO_4$, 60536-62-1; $[Co(phmp)_2Cl_2]ClO_4$, 60489-46-5.

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[12] J. R. Morton and K. F. Preston, *J. Magn. Reson.*, **30**, 577 (1978).

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Crystal and Molecular Structure of $(C_2H_5)_3NH^+[Co(1,2\text{-}C_2B_9H_{11})_2]^-$

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Structural characterizations of a variety of transition-metal dicarbollyl sandwich complexes have been reported.[1] These species have the general formula $(R_2C_2B_9H_9)_2M^n$, where R is H or CH_3 and $-2 \le n \le 0$; in addition, several boron-substituted derivatives have also been crystallographically studied. All of these compounds consist of two icosahedral MC_2B_9 units fused at the metal which is common to both polyhedra, but there are significant variations in cage geometry; different relative orientations of the ligands (rotamers) have been observed, and electron-rich metals such as Ni(II), Ni(III), and Cu(II) cause a type of slip distortion in which the metal is displaced away from the centroid of the five-membered bonding face of the ligand.[1]

Table I. Experimental Parameters and Crystal Data

mol wt	425.93	trans fac (max)	0.93
space group	$Pna2_1$	trans fac (min)	0.87
a, Å	29.048 (9)	2θ range, deg	1.4–50
b, Å	11.457 (4)	reflctn obsd	2076
c, Å	7.100 (2)	reflctn rfnd	1879
V, Å^3	2363	R	0.049
μ, cm^{-1}	7.539	R_w	0.054
D(calcd), g cm^{-3}	1.180	esd unit wt	2.02
A	0.60	Z	4
B	0.35		
cryst dimens (mm from centroid)	100 (0.035)	001 (0.35)	
	$\bar{1}$00 (0.035)	00$\bar{1}$ (0.35)	
	010 (0.09)		
	0$\bar{1}$0 (0.09)		

We wish to report here a structure determination of a bis(dicarbollyl) complex of cobalt(III), $Co(1,2\text{-}C_2B_9H_{11})_2^-$, which was isolated in the course of attempts to prepare mixed-ligand complexes containing $R_2C_2B_4H_4^{2-}$ and $C_2B_9H_{11}^{2-}$ ligands. Salts of $Co(1,2\text{-}C_2B_9H_{11})_2^-$ were prepared long ago by Hawthorne and co-workers,[2] and an X-ray study of the Cs^+ salt was reported by Zalkin, Hopkins, and Templeton;[3] however, the carbon and facial boron atoms were disordered in that study, and hence the ligand orientation could not be established. In the present investigation of the triethylammonium salt, no disorder was encountered and the framework carbon atoms were unambiguously located; this in turn allowed comparison with the known structure[4] of the isoelectronic nickel species, $(1,2\text{-}C_2B_9H_{11})_2Ni^{IV}$.

Experimental Section

Crystals of red $(C_2H_5)_3NH^+[Co(1,2\text{-}C_2B_9H_{11})_2]^-$, obtained by addition of triethylammonium chloride to a reaction mixture containing $(1,2\text{-}C_2B_9H_{11})^{2-}$, $(CH_3)_2C_2B_4H_5^-$, and $CoCl_2$ in tetrahydrofuran, were grown by slow evaporation from 10% acetone in CH_2Cl_2 at 23 °C, and a suitable crystal was mounted on a glass fiber in an arbitrary orientation. The Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections which were used in the program INDEX to obtain an orientation matrix for data collection and to provide approximate cell dimensions. Refined cell dimensions and their estimated standard deviations were obtained from 28 accurately centered reflections. The mosaicity of the crystals was examined by the ω scan technique and judged to be satisfactory. The space group was chosen on the basis of systematic absences, later confirmed by the successful solution and refinement of the structure.

Diffraction data were collected at 295 K on an Enraf-Nonius four-circle DAD-4 diffractometer controlled by a PDP8/M computer using Mo Kα radiation from a highly oriented graphite crystal monochromator (see Table I for data collection parameters). Re-

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[1] Reviews: (a) Dunks, G. B.; Hawthorne, M. F. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1975. (b) Grimes, R. N. *Organomet. React. Synth.* **1977**, *6*, 63. (c) Grimes, R. N. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, in press.

[2] Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.

[3] Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Inorg. Chem.* **1967**, *6*, 1911.

[4] St. Clair, D.; Zalkin, A.; Templeton, D. H. *J. Am. Chem. Soc.* **1970**, *92*, 1173.

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