References

Ansari, M. A., Chau, C.-N., Mahler, C. H. & Ibers, J. A. (1989). *Inorg. Chem.* **28**, 650-654.

Ansari, M. A. & Ibers, J. A. (1990). *Coord. Chem. Rev.* **100**, 223-266.

Christuk, C. C., Ansari, M. A. & Ibers, J. A. (1992). *Inorg. Chem.* **31**, 4365-4369.

Coucouvanis, D. (1991). *Acc. Chem. Res.* **24**, 1-8.

Holm, R. H. & Berg, J. M. (1986). *Acc. Chem. Res.* **19**, 363-370.

Müller, A., Bögge, H., Schimanski, U., Penk, M., Nieradzik, K., Dartmann, M., Krickemeyer, E., Schimanski, J., Römer, C., Römer, M., Dornfeld, H., Wienböker, U., Hellmann, W. & Zimmermann, M. (1989). *Monatsh. Chem.* **120**, 367-391.

Müller, A., Wienböker, U. & Penk, M. (1989). *Chimia*, **43**, 50-52.

Sarkar, S. & Mishra, S. B. S. (1984). *Coord. Chem. Rev.* **59**, 239-264.

Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL92. Program for the Refinement of Crystal Structures*. UNIX β-test version. Univ. of Göttingen, Germany.

Zhu, N., Wu, J., Du, S., Wu, X. & Lu, J. (1992). *Inorg. Chim. Acta*, **191**, 65-68.

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Lithium Bis(tetramethylammonium) Hexanitrocobaltate(III) at 113 and 293 K

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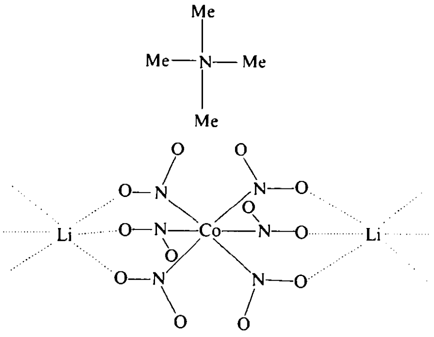
Abstract

The crystal structure of $Li[N(CH_3)_4]_2[Co(NO_2)_6]$ has been determined at 113 and 293 K. The crystals belong to the $P\bar{3}m1$ space group. They are built up of $[Co(NO_2)_6]^{3-}$ octahedra piled along the $\bar{3}$ axes, with the Li^+ ions sandwiched between them at $\frac{1}{2}c$ in an octahedral first coordination sphere involving six symmetry-related O atoms from the nitro groups. Both $[Co(NO_2)_6]^{3-}$ and LiO_6 octahedra exhibit D_{3d} symmetry. On cooling, the unit cell contracts: a 3.21% reduction in volume results from a 1.37% contraction of the *a* edge and a 0.51% contraction of the *c* edge. Bond distances and angles from the two analyses are not significantly different. The two N—O distances of the nitro group differ significantly [1.2421 (5) and 1.2265 (4) Å at 113 K, 1.242 (2) and 1.224 (2) Å at 293 K]. The Co—N bond length of 1.966 (1) Å at 293 K is significantly longer (Δ/σ = 11.8) than the corresponding value [1.9516 (7) Å] in $K_{2-0.36}Na_{1+0.36}[Co(NO_2)_6]$, in which the NO_2^- ion shows C_{2v} symmetry, as a consequence of the differing environments of this anion in the two compounds.

Comment

Fig. 1 shows the interaction of the ions in the crystal, (I), while Fig. 2 shows their packing in the unit cell. The octahedral $[Co(NO_2)_6]^{3-}$ anions lie in columns parallel to the $\bar{3}$ axis with the Co atom at the (0,0,0) symmetry centre; adjacent anions are linked by the Li^+ cation at the $(0,0,\frac{1}{2})$ symmetry centre which is thereby surrounded by an octahedron of O1 atoms. The symmetry of these two octahedra is D_{3d}, and the N1···N1 $(y-x, -x, z)$ and O1···O1 $(y-x, -x, z)$ edges have lengths which differ from those of the N1···N1 $(y, y-x, -z)$ and O1···O1 $(x-y, x, 1-z)$ edges, respectively (see Fig. 2 and Table 2).



(I)

Considering the data of Table 2, it appears that there are no significant differences (*i.e.* >3σ) between corresponding bond lengths and angles at the different temperatures but the Li···O1, O1···O1^{iv} and O2···N2^{i} contacts are significantly shorter at 113 K. The contraction is more pronounced for O2···N2^{i}, in agreement with the fact that the contraction of the *a* unit-cell edge is about 3.4 times larger than that of the *c* edge.

The NO_2^- ion is unsymmetrical (the two N—O distances being significantly different) and lies in a mirror plane which is parallel to the *c* unit-cell edge.

It is interesting to compare the geometry of the complex anion with that of the same anion determined very accurately by Ohba, Toriumi, Sato & Saito (1978) in $K_{2-0.36}Na_{1+0.36}[Co(NO_2)_6]$ at 297 K. In this compound the geometry of the complex anion is T_h (that of the CoN_6 group is O_h). The Co—N distance of 1.9516 (7) Å

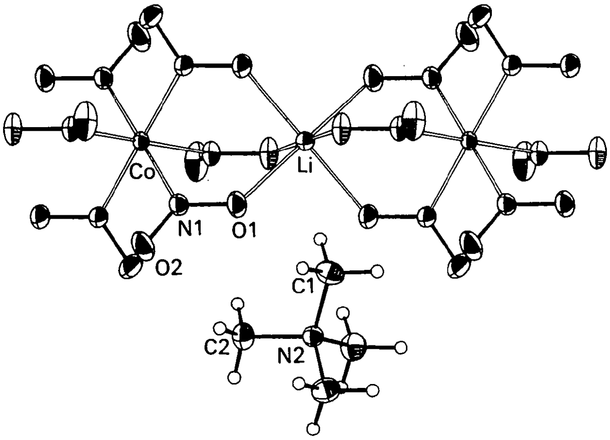


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the structure at 113 K. Ellipsoids are drawn at the 75% probability level.

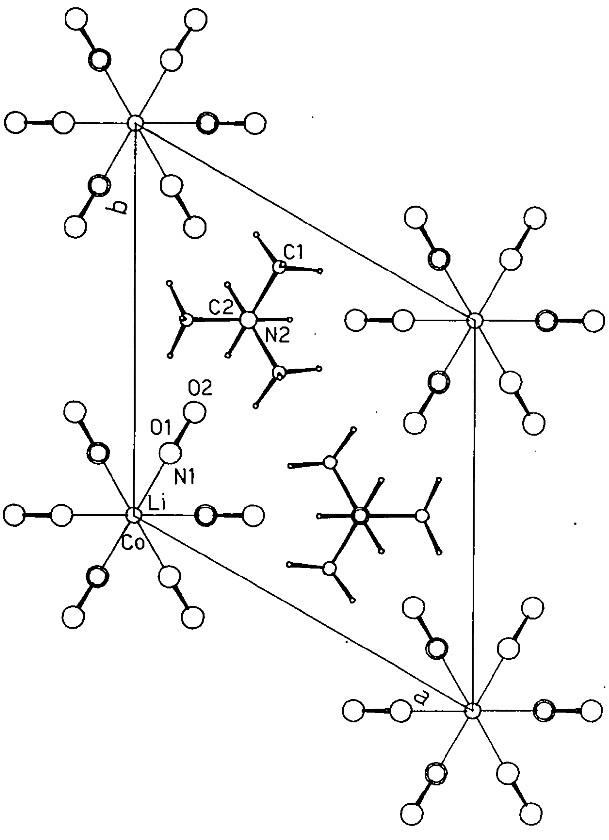
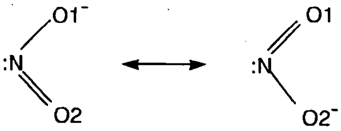


Fig. 2. *PLUTO* (Motherwell & Clegg, 1976) projection of the unit-cell contents onto the *ab* plane.

is significantly shorter than that found in our compound and the NO_2^- group is symmetric with an N—O distance [1.2316 (9) Å] approximately equal to the average N—O distances found here [1.2343 (4) at 113 K and 1.233 (2) Å at 293 K]. These differences indicate that the environment of the NO_2^- ion, in particular the O1···Li and O2···CH_3 interactions, influences not only its orientation but also its distance from the Co atom and its geometry. The O1···Li interaction, which is stronger than the O···Na [2.7619 (7) Å] and O···K [2.9673 (4) Å] interactions owing to the smaller size of the Li^+ cation, can be used to justify the increased Co—N distance found here, while the difference in the interactions involving O1 and O2 explains the lack of symmetry of the NO_2^- ion; the first interaction is much stronger thus making the first of the two resonance structures more important:



Comparison of the values of the O—N—O angle, which is 119.34 (7)° in $K_{2-0.36}Na_{1+0.36}[Co(NO_2)_6]$, shows that this parameter is scarcely influenced by the symmetry of the N—O bonds.

The tetramethylammonium cations are packed along the threefold axes with local non-crystallographic tetrahedral symmetry, surrounded by the O atoms of the anions and forming C—H···O contacts, the shortest of which involve the C1 and O2 atoms (see Table 3). The geometry of this cation is as expected.

From the values of the atomic displacement coefficients (deposited) it appears that cooling reduces thermal motion (static disorder does not seem to be present) by factors of about 2.2 for the non-H atoms and 2.1 for the H atoms. The anisotropic thermal motion is more pronounced in the *xy* plane than in the *z* direction for all of the non-H atoms except the Li^+ ion at 113 K which moves practically isotropically.

Thermal motion analyses of the $[Co(NO_2)_6]^{3-}$ and $[N(CH_3)_4]^+$ ions, carried out in terms of the LST rigid-body model according to Schomaker & Trueblood (1968), considering also internal motions according to Dunitz & White (1973), show that the internal motions are relevant for the O and C atoms, particularly at room temperature. The influence of these motions on the values found for the interatomic distances are not such as to invalidate the above discussion.

Experimental

The compound was obtained by crystallization from an aqueous solution containing $Li_3[Co(NO_2)_6]$ and $[N(CH_3)_4]Cl$ in a 1:2 stoichiometric ratio.

Compound at 113 K

Crystal data

$Li[N(CH_3)_4]_2[Co(NO_2)_6]$
$M_r = 490.20$
Trigonal
$P\bar{3}m1$
$a = 8.856$ (1) Å
$c = 7.017$ (2) Å
$V = 476.6$ (2) Å^3

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 23 reflections
$\theta = 11.23$-$17.39°$
$\mu = 0.979$ mm^{-1}
$T = 113$ (1) K

$Z = 1$
$D_x = 1.708$ Mg m^{-3}

Small pseudo-octahedron
$0.55 \times 0.40 \times 0.39$ mm
Red-brown

Data collection

Enraf-Nonius CAD-4 diffractometer
θ-2θ scans
Absorption correction: spherical
$T_{\min} = 0.732$, $T_{\max} = 0.744$
11 116 measured reflections
3662 independent reflections
3391 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0356$
$\theta_{\max} = 75.23°$
$h = -24 \rightarrow 20$
$k = 0 \rightarrow 24$
$l = -19 \rightarrow 0$
1 standard reflection
frequency: 160 min
intensity variation: within statistical fluctuation

Refinement

Refinement on F^2
$R(F) = 0.0292$
$wR(F^2) = 0.0765$
$S = 1.082$
3653 reflections
45 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 0.0822P]$
where $P = (F_o^2+2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.86$ e Å^{-3}
$\Delta\rho_{\min} = -1.03$ e Å^{-3}

Compound at 293 K

Crystal data

$\mathrm{Li[N(CH_3)_4]_2[Co(NO_2)_6]}$
$M_r = 490.20$
Trigonal
$P\bar{3}m1$
$a = 8.979$ (6) Å
$c = 7.053$ (5) Å
$V = 492.5$ (6) Å^3
$Z = 1$
$D_x = 1.653$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11.13$–$17.20°$
$\mu = 0.948$ mm^{-1}
$T = 293$ (2) K
Small pseudo-octahedron
$0.55 \times 0.40 \times 0.39$ mm
Red-brown

Data collection

Philips PW1100 diffractometer
θ-2θ scans
Absorption correction: spherical
$T_{\min} = 0.732$, $T_{\max} = 0.735$
3086 measured reflections
567 independent reflections
532 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0322$
$\theta_{\max} = 30°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 9$
1 standard reflection
monitored every 100 reflections
intensity variation: within statistical fluctuation

Refinement

Refinement on F^2
$R(F) = 0.0210$
$wR(F^2) = 0.0609$
$S = 1.292$
554 reflections
45 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0180P)^2 + 0.2025P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
113 K				
Co	0	0	0	0.0073 (0)
Li	0	0	1/2	0.0084 (3)
O1	0.10685 (2)	$-x$	0.32944 (4)	0.0145 (1)
O2	0.17751 (2)	$-x$	0.06848 (5)	0.0198 (1)
N1	0.10738 (2)	$-x$	0.15243 (4)	0.0106 (1)
N2	1/3	2/3	0.64143 (8)	0.0104 (1)
C1	0.42522 (3)	$1-x$	0.71239 (8)	0.0167 (1)
C2	1/3	2/3	0.42819 (11)	0.0154 (1)
293 K				
Co	0	0	0	0.0133 (1)
Li	0	0	1/2	0.0143 (13)
O1	0.10570 (8)	$-x$	0.32842 (14)	0.0332 (5)
O2	0.17540 (9)	$-x$	0.07095 (18)	0.0455 (8)
N1	0.10589 (8)	$-x$	0.15229 (16)	0.0199 (4)
N2	1/3	2/3	0.64114 (3)	0.0216 (6)
C1	0.42387 (14)	$1-x$	0.71261 (6)	0.0411 (7)
C2	1/3	2/3	0.42864 (46)	0.0369 (9)

Table 2. *Comparison of bond distances* (Å), *interatomic contacts* (Å), *bond angles* (°) *and torsion angles* (°)

	113 K	293 K	$\lvert\Delta/\sigma\rvert$
Co—N1	1.9639 (3)	1.966 (1)	2.01
O1—N1	1.2421 (5)	1.242 (2)	0.05
O2—N1	1.2265 (4)	1.224 (2)	1.23
N2—C1	1.4949 (4)	1.496 (2)	0.54
N2—C2	1.496 (1)	1.499 (4)	0.73
Li···O1	2.0294 (3)	2.041 (1)	11.11
O2···N2$^{\rm i}$	3.8331 (9)	3.902 (3)	22.00
N1···N1$^{\rm ii}$	2.8529 (4)	2.852 (2)	0.44
N1···N1$^{\rm iii}$	2.6998 (6)	2.707 (2)	3.45
O1···O1$^{\rm ii}$	2.8388 (4)	2.847 (2)	4.02
O1···O1$^{\rm iv}$	2.9010 (7)	2.926 (2)	11.80
Li—O1—N1	126.51 (2)	126.5 (1)	0.10
O1—N1—O2	119.08 (3)	118.1 (1)	9.39
Co—N1—O2	118.30 (2)	118.9 (1)	5.88
Co—N1—O1	122.62 (2)	123.0 (1)	3.73
C1—N2—C2	109.46 (2)	109.7 (1)	2.35
Li—O1—N1—O2	179.92 (3)	−179.8 (1)	2.68
Li—O1—N1—Co	−0.02 (5)	0.2 (2)	1.07

Symmetry codes: (i) $x, y-1, z-1$; (ii) $y-x, -x, z$; (iii) $y, y-x, -z$; (iv) $x-y, x, 1-z$.

Table 3. C—H···O *interaction parameters* (Å, °)

First row, data at 113 K; second row, data at 293 K.

D—H···A	H—A	D···A	D—H···A
C1—H11···O1$^{\rm i}$	2.77 (1)	3.606 (1)	156 (1)
	2.77 (2)	3.675 (3)	155 (2)
$\lvert\Delta/\sigma\rvert$	0.00	21.82	0.45
C1—H12—O2$^{\rm ii}$	2.56 (1)	3.252 (1)	126 (1)
	2.62 (2)	3.308 (3)	125 (1)
$\lvert\Delta/\sigma\rvert$	2.68	17.71	0.45
C2—H21···O1$^{\rm iii}$	2.67 (1)	3.542 (0)	174 (1)
	2.67 (2)	3.610 (2)	173 (1)
$\lvert\Delta/\sigma\rvert$	0.00	34.00	0.71
C2—H21···O2$^{\rm iii}$	2.76 (1)	3.476 (1)	140 (1)
	2.74 (2)	3.521 (3)	141 (1)
$\lvert\Delta/\sigma\rvert$	0.89	14.23	0.71

Symmetry codes: (i) $x-y, x, 1-z$; (ii) $-y, x-y, 1+z$; (iii) $x, 1+y, z$.

The same crystal specimen was used for the two structure determinations. Enraf-Nonius cooling apparatus and liquid nitrogen were used for collecting the low-temperature data. The integrated intensities were measured using a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. Corrections for Lorentz and polarization effects and corrections for absorption [spherical specimen, $\mu R = 0.21$; *International Tables for X-ray Crystallography* (1992), Vol. C, Table 6.3.3.4] were applied to both sets of data. No corrections for extinction were found to be necessary. The structure at 293 K was solved initially using the Patterson method of *SHELXS*86 (Sheldrick, 1985). All of the H atoms were found in a final $\Delta\rho$ map and refined isotropically. The results of the 293 K refinement were used as starting data for the refinement at 113 K. Both structures were refined on F^2 using *SHELXL*92 (Sheldrick, 1993). The thermal-motion analysis was carried out using the *THMV* (Trueblood, 1984) program. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) The calculations were carried out on the Gould Powernode-6040 and ENCORE-91 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma). Data collection: local programs. Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Data reduction: local programs. Program(s) used to solve structure: *SHELXS*86. Program(s) used to refine structure: *SHELXL*92. Molecular graphics: *ORTEP* (Johnson, 1965); *PLUTO* (Motherwell & Clegg, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983); *PARSTCIF* (Nardelli, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Belletti, D., Ugozzoli, F., Cantoni, A. & Pasquinelli, G. (1979). *Gestione on Line di Diffrattometro a Cristallo Singolo Siemens AED con Sistema General Automation Jumbo* 220. Internal Reports 1-3/79. Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

Dunitz, J. D. & White, D. N. J. (1973). *Acta Cryst.* **A29**, 93-94.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580-589.

Motherwell, W. D. S. & Clegg, W. (1976). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95-98.

Nardelli, M. (1992). *PARSTCIF. Program for the Creation of a CIF File from the Output of PARST.* Univ. of Parma, Italy.

Nardelli, M. & Mangia, A. (1984). *Ann. Chim. (Rome)*, **74**, 163-174.

Ohba, S., Toriumi, K., Sato, S. & Saito Y. (1978). *Acta Cryst.* **B34**, 3535-3542.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63-76.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Sheldrick, G. M. (1992). *SHELXL92. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.

Trueblood, K. N. (1984). *THMV. Program for Thermal-Motion Analysis.* Univ. of California, Los Angeles, USA.

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Hexacarbonylcyclopentadienyl-bis-μ-diphenylphosphanido-manganesetungsten, $[MnW(C_{12}H_{10}P)_2(C_5H_5)(CO)_6]$

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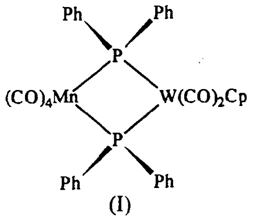
Abstract

Two metal centres in the title compound [hexacarbonyl-$1\kappa^2C,2\kappa^4C$-1(η^5)-cyclopentadienyl-bis(μ-diphenylphosphido-1:2κ^2P)manganesetungsten], Mn and W, are linked *via* two bridging diphenylphosphanido groups. This new four-membered ring, $MnWP_2$, is folded with a large dihedral angle of 27.5 (2)°.

Comment

The title compound, (I), is the first example of a heterometallic $MM'P_2$ ring with Mn and W as metal centres. The Mn atom has four CO groups and the two bridging P atoms as ligands. Its coordination sphere is a slightly distorted octahedron; the sum of the bond angles at the Mn atom in the ring plane is 360°. Regarding the centre of the cyclopentadienyl group (Cp) as the locus of the W—Cp bond, this Cp ligand, two CO groups and the two bridging P atoms surround the W atom with distorted square-pyramidal coordination with the Cp as the apex of the pyramid.



(I)

The Mn···W distance of 3.919 Å is non-bonding, as expected from the electron saturation of the metals: both satisfy the EAN (effective atomic number) rule with 18 valence electrons. The obtuse endocyclic ring angles W—P—Mn [104.9 (1) and 105.5 (1)°] and the acute P—*M*—P angles [69.6 (1) at W, 75.0 (1)° at Mn] are in accordance with the absence of a metal-metal bond. Similar values are known for a great variety of M_2P_2 ring structures (Flörke & Haupt, 1994). The Mn—P distances of 2.384 (4) and 2.390 (4) Å compare well with those found in homometallic Mn_2P_2 rings as in, *e.g.* $[Mn_2(CO)_8(\mu\text{-}PHPh)_2]$, with an average value of 2.358 (2) Å (Flörke