Table 4. V–O *bond lengths* (Å) *in isotypic* $M_3V_2O_8$ *structures*

	$Co_3V_2O_8$ length	$Ni_3V_2O_8$ length	$Mg_3V_2O_8$ length	$Zn_3V_2O_8$ length	Predicted length*	Weighted mean
V–O(1)	1·715 (5)	1·722 (2)	1·716 (1)	1·73 (1)	1·707 (20)	1·720
V–O(2)	1·810 (5)	1·813 (2)	1·809 (1)	1·79 (1)	1·762 (20)	1·810
V–O(3) 2×	1·702 (5)	1·704 (2)	1·695 (1)	1·67 (1)	1·707 (20)	1·697

* Calculated as suggested by Baur from $d_{V-O}=0{\cdot}160\Delta p_o+1{\cdot}721$, where Δp_o is $p_o-\langle p_o\rangle$ with p_o the bond strength of the oxygen atom. The coefficients were determined by Gopal (1972) from 23 accurately refined structures containing tetrahedrally coordinated vanadium; 1·721 represents the grand average V–O bond length.

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Dicarbonylnitrosyltriphenylarsinecobalt(0)

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Abstract. Triclinic, $P\bar{1}$, $a=11{\cdot}286$ (4), $b=10{\cdot}623$ (4), $c=10{\cdot}454$ (5) Å, $\alpha=116{\cdot}53$ (4)°, $\beta=77{\cdot}87$ (4)°, $\gamma=118{\cdot}30$ (4)°, formula $C_{20}H_{15}CoNO_3As$, $Z=2$, $D_x=1{\cdot}53$ g cm^{-3}. The structure consists of discrete molecular units. The coordination around cobalt is approximately tetrahedral and N and C atoms in the nitrosyl and carbonyl groups are disordered.

Introduction. Points of interest in tetracoordinate cobalt nitrosyl complexes lie in the deformation of the tetrahedral coordination in presence of different ligands and in the value of the Co–N–O angle. For this angle, values of 127, 121 and 119° have been reported respectively for $Co(NO)[S_2CN(CN_3)_2]$ (Alderman, Owston & Rowe, 1962), $[CoCl(NO)(en)_2][ClO_4]$ (Snyder & Weaver, 1969) and $[Co(NO)(NH_3)_5]Cl_2$ (Pratt, Coyle & Ibers, 1971). Markedly less bent linkages are reported for different complexes: 170° for $[Co(NO)_2I]_n$ (Dahl, de Gil & Feltham, 1969) and 178° for $Co(NO)(CO)_2PPh_3$ (Albano, Bellon & Ciani, 1972; Ward, Caughlan, Voecks & Jennings, 1972).

Experimental. Crystals of $C_{20}H_{15}CoNO_3As$ were prepared by the method of Innorta, Reichenback & Foffani (1970) from $Co(CO)_3NO$ and $AsPh_3$. A crystal having a cross section 0·20 × 0·11 mm, covered by a collodion film, was mounted along the *c* axis. The unit-cell dimensions were refined by a least-squares fit from the powder pattern. Intensity data were collected from equi-inclination Weissenberg photographs with Fe $K\alpha$ radiation. A combination of the multiple-film and multiple-exposure techniques was used. Intensities were measured by photometric integration of reflexions, integrated one-dimensionally by the Weissenberg camera. Altogether, 1499 reflexions were collected (of which 465 were not observed). The intensities were not corrected for absorption ($\mu=0{\cdot}6$).

Scattering factors were taken from Cromer & Waber (1965). Allowance was made for the $\Delta f'$ and $\Delta f''$ terms of the As and Co atoms. The computations were carried out on a CDC-6600 computer with the X-RAY 71 system of crystallographic programs.

The crystal structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations. The level-by-level scale factors were refined during the isotropic refinement. The N and C atoms in the nitrosyl and carbonyl groups could not be distinguished and were refined as composite

'CN atoms' having a scattering factor $\frac{1}{3}f_N+\frac{2}{3}f_C$. Positions of the H atoms were calculated assuming a C–H bond length of 1·08 Å. Weights for the last cycle were calculated as $w=1/(9{\cdot}0-0{\cdot}75|F_o|+0{\cdot}027|F_o|^2)$. A constant weight of $\frac{1}{5}$ was used for the contributing unobserved reflexions, having $|F_o|<|F_c|$ (80 in the last cycle). The final value of the R index $(R_1=\sum|\Delta|/\sum|F_o|)$ is 0·084. Final atomic coordinates and temperature factors are given in Table 1 and a selection of bond lengths and angles is given in Table 2.*

Discussion. The structure consists of discrete monomeric units without significant intermolecular contacts. An overall view of the molecule is shown in Fig. 1. The coordination symmetry about the Co and As atoms is approximately C_{3v} and the carbonyl–nitrosyl groups nearly eclipse the phenyl groups.

The values of the average angles C–As–C (101·3°) and Co–As–C (116·6°) and the mean As–C bond length (1·93 Å) are comparable with the corresponding values of 101·8°, 116·3° and 1·95 Å obtained for the complex $(Ph_3As)_2Cl_2Rh(\pi\text{-}C_4H_7)$ (Hewitt, de Boer & Anzenhofer, 1970).

The Co–CN and CN–O distances (1·74 and 1·15 Å) and the angles of the distorted cobalt tetrahedron (104·9° for As–Co–CN and 113·6° for CN–Co–CN) are strictly similar to those found in the isomorphous compound $Co(NO)(CO)_2PPh_3$ (Albano, Bellon & Ciani, 1972; Ward, Caughlan, Voecks & Jennings, 1972). The departure of the Co–CN–O angles from 180° is not significant, although the high anisotropic vibration parameters on the CN(3) and O(3) atoms [found also in $Co(NO)(CO)_2PPh_3$] could be a sign of a disordered bent linkage Co–CN–O. This kind of disorder was found in $IrCl_2(NO)(PPh_3)$ for the Co–N–O group (Mingos & Ibers, 1971).

The significant difference between the As–Co–CN and CN–Co–CN angles has been explained for this class of complexes in terms of non-bonding repulsion between ligand orbitals which receive electron density *via* π back-donation in compounds having different accepting abilities (Albano, Bellon, Ciani & Manassero, 1972).

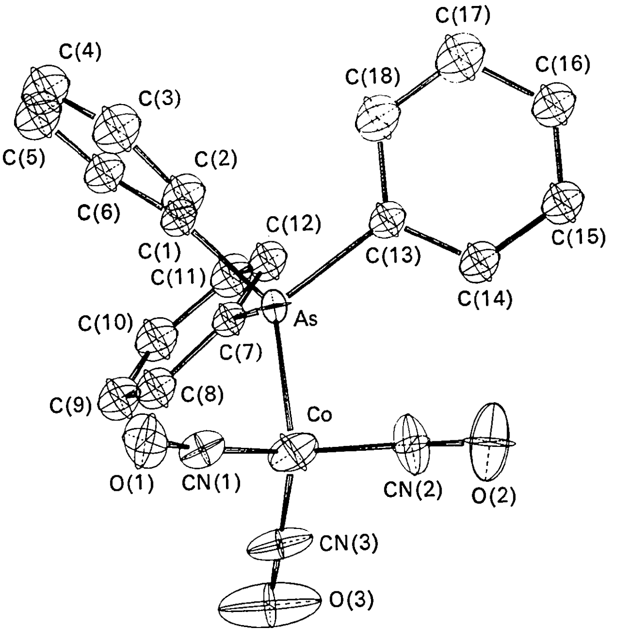

Fig. 1. Molecule of $Co(NO)(CO)_2AsPh_3$, illustrating the thermal parameters at 40% probability.

Table 1. *Positional and thermal parameters of non-hydrogen atoms*

(Thermal parameters (in Å)² have been multiplied by 10². E.s.d.'s are shown in parentheses.)

	x/a	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0·28310 (30)	−0·17965 (40)	0·27839 (36)	6·48 (20)	7·55 (28)	8·37 (30)	3·45 (19)	−1·17 (16)	3·31 (20)
As	0·18223 (16)	−0·11114 (21)	0·16433 (20)	4·11 (10)	3·81 (13)	3·92 (16)	1·71 (8)	−0·12 (7)	1·58 (8)
CN(1)	0·3729 (17)	−0·0055 (22)	0·4223 (21)	6·0 (10)	4·7 (13)	7·2 (15)	2·2 (9)	−0·6 (9)	2·8 (10)
CN(2)	0·3905 (18)	−0·2451 (25)	0·1506 (20)	7·0 (11)	10·6 (17)	5·8 (14)	5·5 (12)	0·8 (9)	1·0 (10)
CN(3)	0·1521 (21)	−0·3219 (29)	0·3266 (26)	6·6 (13)	7·7 (18)	13·3 (21)	2·5 (12)	−1·2 (12)	7·4 (14)
O(1)	0·4333 (15)	0·1112 (20)	0·5079 (16)	9·0 (10)	9·5 (13)	7·4 (12)	5·1 (10)	−1·6 (8)	1·3 (10)
O(2)	0·4656 (17)	−0·2880 (23)	0·0696 (20)	9·5 (12)	13·3 (17)	12·7 (16)	6·6 (12)	−0·2 (10)	1·3 (12)
O(3)	0·0667 (21)	−0·4146 (34)	0·3602 (33)	9·0 (14)	20·2 (29)	29·9 (34)	2·8 (16)	−0·7 (17)	20·8 (28)

	x/a	*y/b*	*z/c*	*U*		*x/a*	*y/b*	*z/c*	*U*
C(1)	0·2301 (16)	0·1063 (20)	0·2372 (18)	4·8 (4)	C(10)	−0·2894 (19)	−0·3098 (24)	0·2039 (22)	6.7 (6)
C(2)	0·3715 (19)	0·2125 (26)	0·2564 (21)	7·1 (6)	C(11)	−0·2319 (19)	−0·3133 (24)	0·0753 (21)	6·6 (6)
C(3)	0·4125 (23)	0·3743 (31)	0·3050 (26)	8·7 (7)	C(12)	−0·0913 (17)	−0·2527 (21)	0·0582 (19)	5·4 (5)
C(4)	0·3168 (23)	0·4279 (28)	0·3404 (25)	8 5 (7)	C(13)	0·2149 (16)	−0·1616 (21)	−0·0383 (19)	4·8 (4)
C(5)	0·1874 (22)	0·3306 (29)	0·3316 (25)	8·2 (6)	C(14)	0·2217 (17)	−0·3011 (22)	−0·1237 (21)	5·7 (5)
C(6)	0·1422 (17)	0·1738 (23)	0·2748 (20)	6·0 (5)	C(15)	0·2438 (18)	−0·3415 (24)	−0·2688 (22)	6·4 (5)
C(7)	−0·0122 (15)	−0·1968 (19)	0·1761 (17)	4·2 (4)	C(16)	0·2620 (19)	−0·2439 (26)	−0·3265 (23)	6·9 (5)
C(8)	−0·0729 (17)	−0·2011 (22)	0·3054 (20)	6·0 (5)	C(17)	0·2592 (22)	−0·0956 (29)	−0·2421 (27)	8·7 (7)
C(9)	−0·2146 (19)	−0·2593 (24)	0·3193 (22)	6·7 (5)	C(18)	0·2314 (21)	−0·0598 (27)	−0·0972 (24)	7·4 (6)

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* A list of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30142 (6pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond distances* (Å) *and angles* (°)

(E.s.d.'s are shown in parentheses.)

Co—As	2·319 (6)
Co-CN(1)	1·758 (16)
Co-CN(2)	1·740 (21)
Co-CN(3)	1·724 (25)
O(1)-CN(1)	1·125 (20)
O(2)-CN(2)	1·167 (29)
O(3)-CN(3)	1·135 (39)
As—C(1)	1·904 (20)
As—C(7)	1·937 (15)
As—C(13)	1·938 (19)
C(1)-C(2)	1·444 (23)
C(2)-C(3)	1·411 (39)
C(3)-C(4)	1·362 (46)
C(4)-C(5)	1·323 (29)
As——Co——CN(1)	105·2 (9)
As——Co——CN(2)	104·5 (10)
As——Co——CN(3)	105·1 (10)
CN(1)-Co——CN(2)	111·6 (8)
CN(1)-Co——CN(3)	114·9 (10)
CN(2)-Co——CN(3)	114·3 (12)
Co——CN(1)-O(1)	175·0 (24)
Co——CN(2)-O(2)	177·1 (24)
Co——CN(3)-O(3)	179·0 (27)
Co——As——C(1)	115·2 (7)
Co——As——C(7)	115·7 (7)
Co——As——C(13)	118·1 (8)
C(1)—As——C(7)	101·1 (8)
C(1)—As——C(13)	101·4 (9)
C(7)—As——C(13)	102·7 (7)
As——C(1)—C(2)	117·6 (18)
As——C(1)—C(6)	126·3 (11)
As——C(7)—C(8)	118·3 (14)
As——C(7)—C(12)	121·5 (13)
As——C(13) -C(14)	118·5 (19)
C(5)—C(6)	1·351 (34)
C(6)—C(1)	1·383 (34)
C(7)—C(8)	1·391 (28)
C(8)—C(9)	1·416 (27)
C(9)—C(10)	1·370 (35)
C(10)-C(11)	1·356 (30)
C(11)-C(12)	1·406 (26)
C(12)-C(7)	1·406 (29)
C(13)-C(14)	1·377 (29)
C(14)-C(15)	1·381 (30)
C(15)-C(16)	1·336 (44)
C(16)-C(17)	1·434 (37)
C(17)-C(18)	1·391 (35)
C(18)-C(13)	1·393 (42)
As——C(13)-C(18)	121·2 (15)
C(1)—C(2)—C(3)	119·8 (24)
C(2)—C(3)—C(4)	118·9 (19)
C(3)—C(4)—C(5)	120·8 (27)
C(4)—C(5)—C(6)	122·8 (28)
C(5)—C(6)—C(1)	121·2 (17)
C(6)—C(1)—C(2)	116·2 (18)
C(7)—C(8)—C(9)	120·0 (20)
C(8)—C(9)—C(10)	118·8 (20)
C(9)—C(10)-C(11)	121·6 (19)
C(10)-C(11)-C(12)	121·2 (20)
C(11)-C(12)-C(7)	118·0 (19)
C(12)-C(7)—C(8)	120·1 (15)
C(13)-C(14)-C(15)	120·1(25)
C(14)-C(15)-C(16)	120·3 (21)
C(15)-C(16)-C(17)	122·0 (23)
C(16)-C(17)-C(18)	116·9 (30)
C(17)-C(18)-C(13)	120·4 (24)
C(18)-C(13)-C(14)	120·3 (19)

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