with those found in the anion trichloro-(*cis*-but-2-ene-1,4-diol)platinate(II) (Colapietro & Zambonelli, 1971). The 2,5-dimethylhex-3-yne-2,5-diol does not appear to exercise a *trans* bond-lengthening effect when coordinated to platinum(II).

Any discussion about the geometry of the acetylenic ligand has no significance considering the low accuracy of the results. As previously mentioned the electron density on the Fourier and difference maps was very diffuse and it was not possible to distinguish the hydroxyl from the methyl groups bound to C(2) and C(5). The isotropic temperature factors of the terminal atoms of the ligand molecule reached very high values, giving no indication about the nature of the atoms. Any choice based on bond-length considerations is not meaningful. On the other hand no short contacts involving the hydroxyl groups, thus providing a criterion to find them, were observed. Any interaction between the hydroxyl groups of the ligand and the platinum or the chlorine atoms (Chatt *et al.*, 1963) may be excluded, because none of the 'carbon' atoms bound to C(2) and C(5) lies sufficiently close to Pt, Cl(1), Cl(2) or Cl(3).

The geometry of the cation $P(C_6H_5)_4^+$ is almost regular.

The technical part of this work was performed by P. Mura.

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Refinement of the Crystal Structures of $Co_3V_2O_8$ and $Ni_3V_2O_8$

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Abstract. $Co_3V_2O_8$ and $Ni_3V_2O_8$, orthorhombic, *Cmca*, $Z=4$ with $a=6·030$ (4), $b=11·486$ (2), $c=8·312$ (5) Å, $D_{calc}=4·693$, $D_{exp}=4·70$ g cm^{-3} and $a=5·936$ (4), $b=11·420$ (6), $c=8·240$ (5) Å, $D_{calc}=4·828$, $D_{exp}=4·87$ g cm^{-3} respectively. Crystals of $Co_3V_2O_8$ were grown from the melt and $Ni_3V_2O_8$ from a KVO_3 flux. These structures, isotypic with that of $Mg_3V_2O_8$, are based upon a cubic closest packing of oxygen atoms with the cations in octahedral sites, showing average M–O bond lengths of 2·093 and 2·089 Å for M=Co, and 2·061 and 2·056 Å for M=Ni. V atoms lie on mirror planes and are tetrahedrally coordinated with mean V–O bond lengths of 1·732 and 1·736 Å for the Co and Ni salts, respectively. These structures differ from those proposed by Fuess, Bertaut, Pauthenent & Durif [*Acta Cryst.* (1970). B**29**, 2036] only in detail; as in $Mg_3V_2O_8$ and $Zn_3V_2O_8$, the longest V–O bond lengths involve the oxygen atom bonded to three cations and the vanadium ion.

Introduction. The intensities and cell dimensions were obtained from a crystal 0·20 × 0·20 × 0·15 mm for $Co_3V_2O_8$ and a ground sphere with a radius of 0·25 mm for $Ni_3V_2O_8$ on a Syntex automatic diffractometer (Mo $K\alpha$, graphite-monochromated, θ–2θ scan with variable scan rate, scintillation counter with pulse height discrimination, a standard reflexion measured every fifty and background determined at both sides of each peak). Absorption and extinction corrections were applied.

Table 1. *Atomic parameters with estimated standard errors*

	x	y	z
(a) $Co_3V_2O_8$			
Co(1)	0	0	0
Co(2)	$\frac{1}{4}$	0·1329 (1)	$\frac{1}{4}$
V	0	0·3773 (1)	0·1204 (1)
O(1)	0	0·2503 (4)	0·2290 (6)
O(2)	0	0·0010 (4)	0·2447 (6)
O(3)	0·2703 (7)	0·1185 (2)	0·9983 (4)
(b) $Ni_3V_2O_8$			
Ni(1)	0	0	0
Ni(2)	$\frac{1}{4}$	0·13024 (3)	$\frac{1}{4}$
V	0	0·37623 (4)	0·11965 (7)
O(1)	0	0·2486 (2)	0·2309 (3)
O(2)	0	0·0013 (2)	0·2448 (3)
O(3)	0·26663 (3)	0·1189 (1)	0·0003 (3)

Data were collected up to $2\theta=70°$ for $Co_3V_2O_8$ and 50° for $Ni_3V_2O_8$ and yielded a total of 664 (507 above

Table 2. *Thermal parameters, with estimated errors*

The definition of the temperature factor is:

$$\exp\left[-2\pi^2(a^{*2}h^2U_{11}+\ldots+2a^*b^*hkU_{12}+\ldots)\right].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(*a*) $Co_3V_2O_8$						
Co(1)	0·0127 (6)	0·0074 (5)	0·0065 (5)	0	0	−0·0002 (4)
Co(2)	0·0101 (4)	0·0055 (4)	0·0080 (4)	0	0·0001 (3)	0
V	0·0105 (5)	0·0032 (4)	0·0057 (4)	0	0	−0·0002 (3)
O(1)	0·0140 (18)	0·0057 (15)	0·0111 (18)	0	0	0·0035 (13)
O(2)	0·0119 (18)	0·0049 (14)	0·0084 (15)	0	0	0·0017 (14)
O(3)	0·0143 (14)	0·0086 (11)	0·0104 (12)	0·0008 (11)	0·0010 (11)	−0·0001 (8)
(*b*) $Ni_3V_2O_8$						
Ni(1)	0·0066 (3)	0·0058 (3)	0·0048 (3)	0	0	−0·0003 (2)
Ni(2)	0·0061 (2)	0·0038 (2)	0·0053 (2)	0	0·0000 (2)	0
V	0·0039 (2)	0·0001 (2)	0·0021 (2)	0	0	0·0002 (3)
O(1)	0·0082 (9)	0·0054 (9)	0·0078 (10)	0	0	0·0018 (8)
O(2)	0·0014 (8)	0·0043 (9)	0·0051 (9)	0	0	0·0014 (3)
O(3)	0·0090 (8)	0·0071 (7)	0·0059 (8)	−0·0011 (5)	0·0008 (5)	−0·0000 (5)

3σ) and 547 (394 above 3σ) unique reflexions, respectively, whose intensity measure was positive. The systematic absences are hkl with $h+k$ odd, $h0l$ with l odd and $hk0$ with h odd. Trial parameters were the final parameters for $Mg_3V_2O_8$ (Krishnamachari & Calvo, 1971). Full-matrix least-squares refinement with anisotropic thermal parameters and weights chosen so that $\omega(|F_o|-|F_c|)^2$ would be independent of F_o yielded final R values of 0·057 and 0·028 for $Co_3V_2O_8$ and $Ni_3V_2O_8$ respectively. The atomic parameters are listed in Tables 1 and 2.*

Discussion. The structures of $Co_3V_2O_8$ and $Ni_3V_2O_8$ are isotypic with those of $Mg_3V_2O_8$ (Krishnamachari & Calvo, 1971) and $Zn_3V_2O_8$ (Gopal & Calvo, 1971). Note that the x coordinate of O(3) in the latter paper should be 0·2778. Tables 3 and 4 contain the pertinent bond lengths and angles. The cation polyhedra in both crystals are similarly distorted. The four M(1)–O(3) bonds generated by the $2/m$ symmetry at M(1) are significantly longer than the axial M(1)–O(2) bond lengths. The M(2)–O(2) bonds are the longer of the three sets of symmetry independent bonds around M(2) and the M(2)–O(1) one shortest. The V–O bond lengths, compared with those in $Mg_3V_2O_8$ and $Zn_3V_2O_8$ in Table 4, range from 1·702 to 1·813 Å. The longest V–O bond involves that oxygen atom shared between three cations and the vanadium ion while the remaining ones are shared between only two cations and the vanadium ion. The O–V–O bond angles, except for O(3)*g*–V–O(3)*i*, do not deviate significantly from ideality. All four structures show the same V–O bond lengths within 3σ and therefore the weighted mean V–O bond lengths over the four compounds are also given in Table 4. The deviation between the predicted value, using $d_{V-O}=0{\cdot}160\Delta p_0+1{\cdot}721$, and the weighted mean is greatest for the longest bond. It is not unexpected that the linear correlation predicted by Baur (1970) would break down as the distortion increases. In contrast the V–O(1) and V–O(2) values determined by Fuess, Bertaut, Pauthenet & Durif (1970) by combining powder neutron and X-ray diffraction are 1·78 (3) and 1·67 (3) Å ($Co_3V_2O_8$) and 1·82 (4) and 1·72 (3) Å ($Ni_3V_2O_8$) respectively.

Table 3. *Bond lengths and angles, with estimated standard errors, for* $Co_3V_2O_8$ *and* $Ni_3V_2O_8$

	Co	Ni	
M(1)–O(2)*a*,*b*	2·031 (5) Å	2·017 (2) Å	2×
M(1)–O(3)*a*,*b*,*d*,*e*	2·124 (5)	2·084 (2)	4×
M(2)–O(1)*a*,*g*	2·032 (3)	2·013 (2)	2×
M(2)–O(2)*a*,*g*	2·137 (3)	2·091 (2)	2×
M(2)–O(3)*a*,*h*	2·099 (4)	2·064 (2)	2×
V–O (see Table 4)			
O(2)*a*–M(1)–O(3)*a*	89·8 (3)°	89·66 (7)°	
O(3)*a*–M(1)–O(3)*b*	79·7 (2)	81·34 (7)	
O(1)*a*–M(2)–O(1)*h*	96·8 (2)	95·64 (7)	
O(1)*a*–M(2)–O(2)*a*	86·8 (3)	87·04 (7)	
O(1)*a*–M(2)–O(2)*g*	175·1 (2)	175·90 (9)	
O(1)*a*–M(2)–O(3)*h*	95·4 (3)	94·88 (8)	
O(1)*a*–M(2)–O(3)*a*	90·6 (3)	89·94 (8)	
O(2)*a*–M(2)–O(2)*g*	89·9 (1)	90·46 (7)	
O(2)*a*–M(2)–O(3)*a*	88·0 (3)	88·21 (8)	
O(3)*a*–M(2)–O(3)*c*	171·0 (1)	172·82 (7)	
O(1)—V–O(2)*a*	110·0 (2)	109·79 (11)	
O(1)—V–O(3)*f*	109·2 (2)	109·66 (7)	
O(2)*c*–V–O(3)*f*	109·7 (2)	109·37 (7)	
O(3)*g*–V–O(3)*i*	109·1 (3)	108·97 (10)	

Symmetry transformations

(*a*) x, y, z; (*b*) $-x, -y, z$; (*c*) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (*d*) $-x, -y, -z$; (*e*) $x, y, -z$; (*f*) $-x, \frac{1}{2}-y, \frac{1}{2}+z$; (*g*) $\frac{1}{2}-x, y, \frac{1}{2}+z$; (*h*) $\frac{1}{2}-x, y, \frac{1}{2}-z$; (*i*) $-x, \frac{1}{2}-y, \frac{1}{2}-z$.

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* A table of observed and calculated structures has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30144 (5pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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 $d_{V-O}=0\cdot160\Delta p_0+1\cdot721$, 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, $P\bar{1}$, $a=11\cdot286$ (4), $b=10\cdot623$ (4), $c=10\cdot454$ (5) Å, $\alpha=116\cdot53$ (4)°, $\beta=77\cdot87$ (4)°, $\gamma=118\cdot30$ (4)°, formula $C_{20}H_{15}CoNO_3As$, $Z=2$, $D_x=1\cdot53$ 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 ($\mu=0\cdot6$).

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