N1—Cd—N1^{i}	69.2 (3)	C6—N2—Cd	155.4 (4)
N1—Cd—N2	130.7 (2)	N1—C1—C2	122.8 (7)
N1^{i}—Cd—N2	94.2 (2)	C3—C2—C1	117.4 (8)
N1—Cd—N2^{i}	94.2 (2)	C2—C3—C4	120.6 (8)
N1^{i}—Cd—N2^{i}	130.7 (2)	C3—C4—C5	119.8 (8)
N2—Cd—N2^{i}	127.8 (2)	N1—C5—C4	120.2 (6)
N1—Cd—S1	92.34 (14)	N1—C5—C5^{i}	116.4 (4)
N1^{i}—Cd—S1	129.79 (13)	C4—C5—C5^{i}	123.4 (5)
N2—Cd—S1	62.55 (13)	C7—C6—N2	126.1 (6)
N2^{i}—Cd—S1	95.57 (12)	C7—C6—C11	119.6 (7)
N1—Cd—S1^{i}	129.79 (13)	N2—C6—C11	114.3 (6)
N1^{i}—Cd—S1^{i}	92.34 (14)	C8—C7—C6	118.5 (7)
N2—Cd—S1^{i}	95.57 (12)	C7—C8—C9	122.1 (7)
N2^{i}—Cd—S1^{i}	62.55 (13)	C10—C9—C8	119.8 (7)
S1—Cd—S1^{i}	131.15 (8)	C9—C10—C11	119.0 (7)
C12—S1—Cd	81.3 (2)	C10—C11—C6	120.9 (6)
C11—S2—C12	90.2 (3)	C10—C11—S2	129.5 (5)
C1—N1—C5	119.0 (6)	C6—C11—S2	109.6 (5)
C1—N1—Cd	122.0 (5)	N2—C12—S1	123.8 (5)
C5—N1—Cd	119.0 (5)	N2—C12—S2	113.9 (5)
C12—N2—C6	112.1 (5)	S1—C12—S2	122.4 (4)
C12—N2—Cd	92.3 (4)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The data were collected using a variable scan speed of 4.19–29.3° min^{-1} (Siemens, 1991). The structure was solved through a combination of direct methods and difference Fourier synthesis, using the *SHELXTL* program package (Sheldrick, 1991). Refinement was performed with *SHELXL*93 (Sheldrick, 1993) on F^2 using the whole data set. H atoms were included at their expected positions, with fixed displacement parameters.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the IUCr (Reference: AB1143). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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On the Structure of the Mixed Ligand Complex of $[VO]^{2+}$ with Hydrotris(3,5-dimethylpyrazolyl)borato and 1,3-Diphenyl-1,3-propanedionato Ligands

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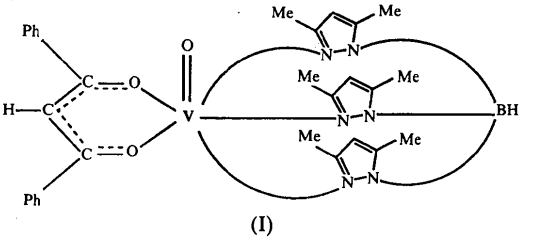
Abstract

The structure of (1,3-diphenyl-1,3-propanedionato-κ^2O,O')oxo[tris(3,5-dimethyl-1-pyrazolyl-κN^2)hydroborato]vanadium(IV) methyl cyanide, $[VO(C_{15}H_{22}BN_6)(C_{15}H_{11}O_2)].xCH_3CN$, has recently been described and refined [Beddoes, Eardley, Mabbs, Moorcroft & Passand (1993). *Acta Cryst.* C**49**, 1923–1926] in space group $Pna2_1$ (orthorhombic; a = 15.960 (1), b = 12.447 (1), c = 17.044 (1) Å, Z = 4). It is better described in *Pnma* (conventional setting of *Pnam*). Revised coordinates are given and the anomalous bond lengths reported earlier are revised.

Comment

In their report of the structure of $[VO(C_{15}H_{22}BN_6)(C_{15}H_{11}O_2)].xCH_3CN$, (I), described and refined in space group $Pna2_1$, the authors (Beddoes, Eardley, Mabbs, Moorcroft & Passand 1993; hereinafter,



(I)

BEMMP) reported that the two, presumably equivalent, C—O bonds in the propanedionato group have very different lengths, 1.183 (12) and 1.382 (14) Å, as do the C—C bonds in these groups, 1.287 (18) and 1.472 (17) Å; C—N distances in the pyrazolyl groups (not all are listed by BEMMP) range from 1.26 to 1.45 Å. They also noted 'suspect bond lengths in the regions of the phenyl groups', which prompted them to collect data from two separate crystals and, even-

† Contribution No. 8918.

tually, to treat the phenyl groups as rigid bodies with prescribed geometries. Since such problems are typical of attempts to refine a centrosymmetric structure in a non-centrosymmetric space group, further refinement in *Pnma* seemed appropriate. This refinement was based on the 2446 F_o values recovered from SUP 71341 and proceeded to an R of 0.059 for 217 parameters, compared to the 0.074 for 286 parameters reported by BEMMP. The heavier atoms of the main molecule were refined with anisotropic U_{ij} values and those of the MeCN group with isotropic B values. H atoms were assigned calculated positions (C—H 0.95, B—H 1.00 Å) with the help of difference maps, which indicated that all four independent methyl groups (of the pyrazolyl groups) are oriented with one H atom eclipsed relative to the central C—H group; they were not adjusted further. I included an occupancy parameter for the CH_3CN molecule, which lies in a large cavity and is disordered across a mirror plane; the final value was 0.85 (2) (BEMMP report an occupancy of '*ca* 0.5'). Both the CH_3CN molecule and the surrounding phenyl ring C(51)–C(56) show large displacement coefficients. In the final full-matrix least-squares cycle, the maximum shift was 0.03σ; the largest features in a difference map, at about ± 0.45 e Å^{-3}, were near the V atom. Resulting coordinates are given in Table 1. They lead to entirely reasonable bond lengths and angles, with the pairs of C—O and C—C distances in the propanedionato groups equal (by symmetry) at 1.276 (4) and 1.393 (6) Å; the four independent C—N bond lengths are statistically equal, at 1.347 (2) Å. The two independent V—N distances are 2.319 (4) and 2.096 (2) Å, indicating the strong *trans* influence of the coordinated O atom, as noted by BEMMP.

In selecting space group $Pna2_1$ over *Pnma*, BEMMP were influenced by intensity statistics, which 'favour the non-centrosymmetric space group'. This erroneous indication undoubtedly resulted from the omission of the weak reflections in calculating the statistics; as has been noted previously (*e.g.* Marsh, 1981), intensity distributions obtained from a subset of data which contains only the stronger reflections are systematically biased toward a non-centrosymmetric indication. In the present case, the curve obtained from the 2446 reflections in SUP 71341 follows very closely the non-centrosymmetric curve predicted by Howells, Phillips & Rogers (1950); however, when I added – with very small F_o values – 1030 reflections that were within the sphere of data but not included in SUP 71341 (and all of which had small F_c values), the resulting distribution curve was very close to that predicted for a centrosymmetric structure. The curves are similar to those shown in Fig. 1 of Marsh (1981); a capsule summary of the intensity statistics is given in Table 2.

As in all cases of this type, with the truncated data at hand it is impossible to assert conclusively that the structure conforms to space group *Pnma*; small distortions – conceivably as large as might result from an ordering of the MeCN solvent molecules – would be undetectable in the absence of the weak reflections. As has been said by so many people so many times: removing the weak reflections also removes the possibility of differentiating between a centrosymmetric structure and one that is only approximately centrosymmetric. In addition, as in the present case, removing the weak reflections may so distort the intensity statistics as to convince the experimentalist that the structure is non-centrosymmetric even when the remaining, stronger reflections are entirely compatible with a centrosymmetric structure. Journals publishing reputable crystallographic results should insist that all reflections be retained throughout a structure analysis.

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

Space group *Pnma*; $a = 15.960$, $b = 17.044$, $c = 12.447$ Å. Atom numbering is from BEMMP.

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

	x	y	z	U_{eq} or B
V	0.0897 (0.5)	0.2500	0.1494 (0.6)	0.0364 (2)
O(1)	0.0162 (2)	0.2500	0.0631 (3)	0.0525 (9)
N(11)	0.1886 (2)	0.2500	0.2859 (3)	0.0363 (9)
N(12)	0.1605 (2)	0.2500	0.3903 (3)	0.0382 (9)
N(21)	0.0352 (2)	0.3350 (1)	0.2490 (2)	0.0390 (6)
N(22)	0.0281 (2)	0.3235 (1)	0.3586 (2)	0.0386 (6)
B	0.0658 (3)	0.2500	0.4107 (4)	0.0412 (13)
C(11)	0.2726 (3)	0.2500	0.2925 (4)	0.0429 (12)
C(12)	0.2974 (3)	0.2500	0.4003 (5)	0.0516 (14)
C(13)	0.2252 (3)	0.2500	0.4602 (4)	0.0484 (12)
C(14)	0.3272 (3)	0.2500	0.1974 (5)	0.0644 (16)
C(15)	0.2138 (4)	0.2500	0.5793 (5)	0.0768 (17)
C(21)	−0.0054 (2)	0.4022 (2)	0.2267 (3)	0.0500 (9)
C(22)	−0.0373 (2)	0.4331 (2)	0.3211 (3)	0.0600 (10)
C(23)	−0.0160 (2)	0.3832 (2)	0.4018 (3)	0.0492 (8)
C(24)	−0.0124 (3)	0.4330 (2)	0.1159 (3)	0.0773 (12)
C(25)	−0.0354 (3)	0.3874 (3)	0.5191 (3)	0.0757 (11)
O(41)	0.1622 (1)	0.3306 (1)	0.0790 (2)	0.0424 (5)
C(41)	0.1992 (2)	0.3224 (2)	−0.0112 (3)	0.0413 (7)
C(42)	0.2155 (3)	0.2500	−0.0590 (4)	0.0495 (12)
C(51)	0.2593 (4)	0.3993 (2)	−0.1644 (3)	0.0946 (15)
C(52)	0.2870 (4)	0.4704 (3)	−0.2070 (4)	0.1177 (19)
C(53)	0.2857 (3)	0.5364 (3)	−0.1506 (5)	0.0947 (16)
C(54)	0.2579 (4)	0.5329 (3)	−0.0492 (5)	0.1154 (20)
C(55)	0.2296 (3)	0.4631 (2)	−0.0052 (4)	0.0913 (15)
C(56)	0.2292 (2)	0.3962 (2)	−0.0619 (3)	0.0468 (8)
C(1)†	0.3990 (10)	0.2666 (15)	0.7405 (12)	12.4 (6)‡
C(2)†	0.4562 (11)	0.2184 (9)	0.7075 (12)	10.3 (5)‡
N(3)†	0.5131 (12)	0.1712 (12)	0.6861 (14)	17.0 (7)‡

† Number in cell: 3.42 (7).
‡ Isotropic displacement parameter, B.

Table 2. *Some theoretical and observed intensity averages*

	I[a]	I[b]	Strong[c]	All[d]
$\langle \lvert E \rvert \rangle$	0.886	0.798	0.896	0.821
$\langle E^2 \rangle$	1.000	1.000	1.000	1.000
$\langle \lvert E^2 - 1 \rvert \rangle$	0.736	0.968	0.714	0.925

Notes: (*a*) Theoretical, non-centrosymmetric; (*b*) theoretical, centrosymmetric; (*c*) observed, 2446 strong reflections; (*d*) observed, 3476 total reflections (see text).

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