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PSEUDOSYMMETRIC MOLECULAR SHAPE RESULTING IN DISORDER IN THE CRYSTALLINE STATE[+]

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The structures of $[(C_4Me_4)NiL]PF_6$ and $[(C_5Me_5)CrL]PF_6$ where L is the tripod ligand $[\eta^3\text{-}CpCo\{P(O)(OEt)_2\}_3]^-$ were determined by single crystal X-ray diffraction studies. The cations are expected to have point symmetry 1 (C_1) or *m* (C_s); in the crystal they show apparent *2mm* (C_{2v}) symmetry and are disordered. An explanation for this behaviour is offered by the fact that these molecules have a pseudosymmetric shape. An approach for visualizing the shape and packing of medium-sized molecules is presented.

Introduction

Disorder affecting all or the vast majority of the atoms in organometallic or coordination compounds is rare. Recently, in our laboratory the disorder problem in the structure of $Me_3Sn\text{-}V(CO)_6$ was solved [1] where the geometric shape and the space filling properties of the molecule seem to allow for the observed end-for-end disorder. In this paper we present a related problem that we encountered in the structure determination of two complexes with the tripod ligand $L=[CpCo\{P(O)(OEt)_2\}_3]^-$. Anions of this type have been shown to be versatile tridentate ligands [2]. The cations $[(C_4Me_4)NiL]^+$ and $[(C_5Me_5)CrL]^+$ were prepared as model compounds for the *aqua* complexes $[(C_4Me_4)Ni(H_2O)_3]^{2+}$ and $[(C_5Me_5)Cr(H_2O)_3]^{2+}$, respectively. The synthetic interest in these systems stems from the fact that only relatively few compounds containing organometallic fragments and water as a σ-donor ligand are well characterized [3–5].

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Experimental

Synthesis of [(C_4Me_4)NiL]PF_6, **1**, *and [(C_5Me_5)CrL]PF_6*, **2**

The compounds were prepared from the corresponding halides $[(C_4Me_4)NiCl_2]_2$ and $[(C_5Me_5)CrCl_2(THF)]$, respectively, by halide abstraction with $AgBF_4$ in aqueous solution. Subsequently, the intermediate *aqua* complexes were reacted with the sodium salt of the tripod ligand to give the corresponding monocations. These were precipitated from the aqueous solution with an excess of NH_4PF_6. The salts so obtained were collected by filtration and dried *in vacuo*. Compound **1** exhibits an NMR spectrum in accord with the formula whereas **2** shows broad absorptions due to its paramagnetism. Single crystals were obtained by slow diffusion of pentane into an acetone solution.

X-ray diffraction experiments

The structure determinations were carried out on an ENRAF-Nonius CAD4 diffractometer equipped with a graphite monochromator. Experimental conditions for intensity data collection are given in Table I together with the crystal data. For the structure solution and refinement, the SDP [6] and SHELXS-86 [7] programs were used.

Table I

Crystal data and parameters for structure solution in compounds **1** *and* **2**

		1	**2**
Space group (No.)		*P*4_2/*ncm* (138)	*P*4_2/*ncm* (138)
Crystal data	a	13.134(3) Å	13.269(9) Å
	c	21.807(3) Å	21.748(8) Å
	V	3762(2) Å^3	3829(7) Å^3
	Z	4	4
	d_{calc}	1.496 g cm^{-3}	1.505 g cm^{-3}
	μ	11.8 cm^{-1}	9.5 cm^{-1}
Data collection		Mo K_α	Mo K_α
	T	298 K	243 K
	θ	3-24°	3-31°
		ω-scan	ω-scan
Measured reflections		2927	3887
Observed indep. refl.		1038 ($I>2\sigma(I)$)	1141 ($I>3\sigma(I)$)
Parameters refined		103	118
Agreement factors	R	0.091	0.064
	R_w	0.093	0.072 $w=1/\sigma^2(F_o)$

Structure determinations

Crystals of compound **1** are dark red, quadratic platelets, some of them revealing their ditetragonal dipyramidal habitus on closer inspection. The extinction symbol *Pnc* suggested space group $P4_2/ncm$, no. 138, which was in accord with the crystal morphology. The unit cell dimensions (Table I) and the approximate molecular volume of 900 – 1000 Å^3 resulted in a unit cell content of four molecules. No accord between site symmetries for $Z=4(222, \bar{4}, 2/m$ or $2mm)$ and molecular symmetry (*m* at most) could be found. However, as detailed further below, the solution became possible after the successful determination of the crystal structure of **2**.

Crystals of **2** exhibit a very different morphology. Most of them are elongated black rods and they do not show apparent fourfold symmetry. The long axis of the rods was found to be perpendicular to the *c* axis of the tetragonal unit cell. Cell dimensions (Table I) were very similar to those found for **2**, and the data set showed the same reflection conditions. Space group was $P4_2/ncm$ (no. 138, the second setting with origin on **1** was used). In addition to the independent intensity data $(+h, +k, +l, k \geq h)$ a limited set of 800 reflections was collected on half the reflection sphere $(+h, \pm k, \pm l)$ and symmetry equivalent reflections were averaged. They showed intensity variations of ±1.5 % under the Laue class $4/mmm$. The metal atoms (Co, Cr) were found to be located on special positions **4e**, corresponding to a $2mm$ site symmetry for the cation.

Figure 1 is a SCHAKAL [8] plot of the tripod ligand. Figure 2 gives a schematic representation of the resulting disorder: while mirror plane *m* is contained in the molecule, mirror plane *m'* generates an alternative orientation of the cation.

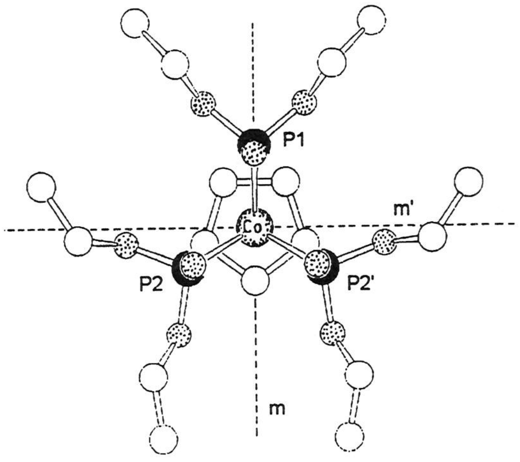

Fig. 1. SCHAKAL representation of the tripod ligand in **2**

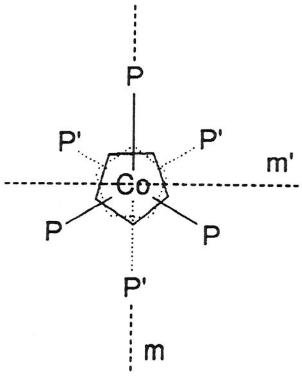

Fig. 2. Illustration of disorder in the cations of **1** and **2**

After refinement of the metal atoms all of the remaining disordered non-hydrogen atoms in the cation could be located in difference Fourier syntheses and refined with appropriate multiplicities.

Figure 3 shows an ORTEP representation of the cation (disorder in the tripod ligand is omitted for clarity).

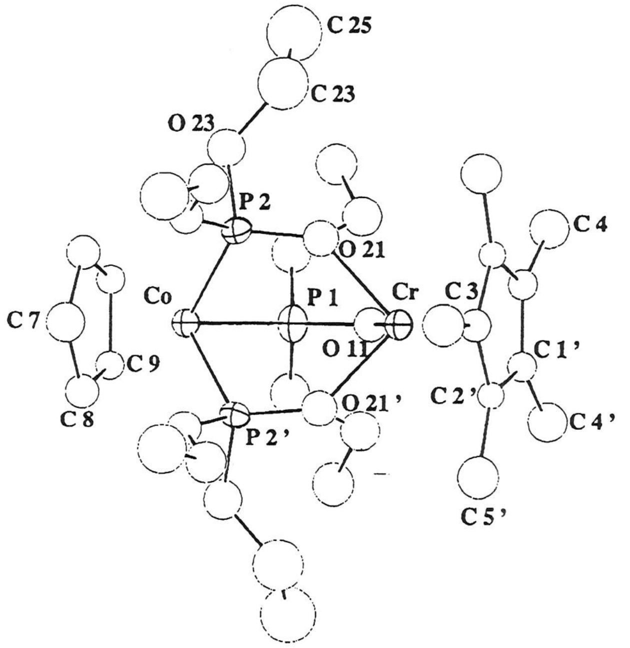

Fig. 3. ORTEP plot of the cation in **2**. Ellipsoids are drawn at 30% probability

No disorder problems arose for the anion. Its phosphorus atom occupies the special position **4a** with point symmetry 222 (D_2), a subgroup of the point group of the octahedron. Anisotropic refinement of the metal, phosphorus, and fluorine atoms, isotropic refinement for the remaining non-hydrogen atoms and unrefined hydrogen atoms in structure factor calculations gave the convergence results shown in Table I. Fractional co-ordinates and isotropic displacement parameters are given in Table II.

Table II

Fractional co-ordinates and displacement parameters for compound **1**

Atom	*x*	*y*	*z*	B(*iso*)
Ni	0.250	0.250	0.4448(1)	4.62(3)
Co	0.250	0.250	0.2714(1)	4.15(3)
P1	0.3478(4)	0.152	0.3278(3)	5.1(1)
P2	0.1219(4)	0.2138(4)	0.3273(2)	5.0(1)
P3	0.250	0.750	0.000	8.2(1)
F1	0.3329(5)	0.667	0.000	12.4(3)
F2	0.1887(8)	0.6913(7)	0.0493(4)	16.4(3)
O11	0.340(1)	0.160	0.3961(9)	6.4(5)*
O12	0.461(1)	0.1689(9)	0.3099(6)	5.8(3)*
O21	0.1306(9)	0.2176(9)	0.3965(5)	5.8(3)*
O22	0.029(1)	0.276(1)	0.3070(6)	6.8(3)*
O23	0.0719(9)	0.1138(9)	0.3072(5)	6.9(3)*
C1	0.2496(7)	0.3235(6)	0.5241(4)	7.0(3)*
C2	0.253(1)	0.435(1)	0.5275(9)	18.4(7)*
C7	0.315(1)	0.315	0.194(1)	4.0(5)*
C8	0.334(1)	0.215(1)	0.1935(6)	3.7(4)*
C9	0.236(1)	0.154(1)	0.1939(8)	6.0(5)*
C12	0.541(2)	0.144(2)	0.353(1)	10.1(8)*
C14	0.634(1)	0.143(2)	0.3130(8)	7.1(5)*
C22	−0.051(1)	0.305(1)	0.3430(9)	6.2(5)*
C23	0.021(3)	0.035(3)	0.345(2)	21(1)*
C24	−0.106(2)	0.402(2)	0.336(1)	11.1(8)*
C25	0.049(3)	−0.044(3)	0.364(2)	20(2)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\,[a^2\,\beta(1,1) + b^2\,\beta(2,2) + c^2\,\beta(3,3)]$

After the successful refinement of **2**, the data set of **1** was tackled again. The atomic positions of the $MLPF_6$ moiety of structure **2** were used as a starting model for **1**. After refinement the remaining non-hydrogen atoms of the model (the carbon atoms of the C_4Me_4 ligand) were located in a difference Fourier map. They showed no disorder and completed the structure model, albeit the displacement parameters for C2 were rather large. Table III contains the refined atomic co-ordinates and displacement parameters. For both compounds **1** and **2**, selected interatomic distances and angles are presented in Table IV.

Table III

Fractional co-ordinates and displacement parameters for compound 2

Atom	*x*	*y*	*z*	B(*iso*)
Co	0.250	0.250	0.27019(6)	3.18(2)
Cr	0.250	0.250	0.44594(7)	3.42(2)
P1	0.3464(2)	0.154	0.3281(2)	3.99(9)
P2	0.1219(2)	0.2150(2)	0.3258(1)	3.81(6)
P3	0.250	0.750	0.000	5.29(5)
F1	0.3344(3)	−0.334	0.000	8.6(1)
F2	0.1893(4)	−0.3088(4)	0.0506(2)	9.8(1)
O11	0.3367(6)	0.163	0.3957(5)	4.4(2)*
O12	0.4591(7)	0.1640(7)	0.3105(4)	6.3(2)*
O21	0.1324(6)	0.2177(6)	0.3942(3)	5.1(2)*
O22	0.0311(6)	0.2825(6)	0.3088(3)	4.6(2)*
O23	0.0747(6)	0.1122(6)	0.3076(3)	5.8(2)*
C1	0.2589(8)	0.1701(8)	0.5332(4)	3.4(2)*
C2	0.1618(7)	0.2157(7)	0.5304(4)	2.8(2)*
C3	0.1785(9)	0.321	0.5303(7)	4.1(3)*
C4	0.273(1)	0.056(1)	0.5345(6)	6.2(3)*
C5	0.059(1)	0.172(1)	0.5300(6)	6.6(4)*
C6	0.097(1)	0.403	0.5301(9)	6.2(5)*
C7	0.189(1)	0.311	0.1913(8)	5.5(4)*
C8	0.2921(8)	0.3299(8)	0.1921(4)	4.3(2)*
C9	0.3405(8)	0.2350(7)	0.1921(4)	3.2(2)*
C12	0.540(1)	0.150(1)	0.3533(6)	6.0(3)*
C14	0.638(1)	0.149(1)	0.3165(6)	7.0(3)*
C22	−0.052(1)	0.303(1)	0.3434(7)	6.6(3)*
C23	0.023(1)	0.049(1)	0.3519(6)	10.0(4)*
C24	−0.114(1)	0.389(1)	0.3297(7)	9.3(5)*
C25	0.042(2)	−0.058(2)	0.3415(9)	12.2(6)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\,[a^2\,\beta(1,1) + b^2\,\beta(2,2) + c^2\,\beta(3,3)]$

Table IV

Selected interatomic distances (Å) and angles (°) in **1** *and* **2**

	1*	**2***
M – R (best plane)	1.730	1.864
M – O11	1.987(8)	1.959(5)
M – O21	1.936(7)	1.971(6)
Co – P1	2.195(3)	2.204(2)
Co – P2	2.132(3)	2.138(2)
P1 – Co – P2	90.6(1)	90.71(9)
P2 – Co – P2'	91.4(2)	91.42(9)

* 1: M = Ni, R = C_4Me_4; 2: M = Cr, R = C_5Me_5

Molecular shape

What is the origin of the orientational disorder of the cations in 1 and 2? We note that this disorder affects the majority of the atoms of the cations of both 1 and 2 while several other structures with similar tridentate ligands are known which do not show signs of disorder [9 – 11]. For more insight let us reconsider the crystal structure of Me_3Sn-$V(CO)_6$ which may serve as a less involved example. In this case the shape of the molecule is close to that of a rugby-ball. While the molecular symmetry is *3mm* (C_{3v}) the shape is pseudosymmetric with respect to a non-crystallographic mirror operation perpendicular to the Sn-V bond. Thus the shape of the molecule allows for the observed end-for-end disorder [1].

In order to look for pseudosymmetry in molecules we decided to abstract from the individual atoms and to visualize molecular shape by a convex polyhedron enveloping the molecule in question. Note that this approach is entirely geometric in nature. Atoms are treated as spheres with appropriate van der Waals radii. The faces of the enveloping polyhedron are constructed as planes tangential to the peripheral atoms, its vertices result from the intersection of these planes and are close to the peripheral atoms. Evidently, the resulting geometric object conveys less information than a space-filling or ball-and-stick model, but due to its higher degree of abstraction it may easily be rotated, subjected to symmetry operations or superimposed to other polyhedra without becoming confusing.

Our implementation of the above mentioned approach consists of two computer programs. The first (POLYMOL) is interfaced for convenience to standard parameter files containing lattice constants, symmetry operations, and fractional coordinates. Van der Waals radii for the different atom types are defaulted, but may be changed interactively. The resulting convex polyhedron is output to a graphics display and can be input to the second program (POLYPAC) which allows to manipulate and pack one or more polyhedra interactively.

Results

To examine the cations $[(C_4Me_4)NiL]^+$ and $[(C_5Me_5)CrL]^+$ in terms of their molecular shape, we used a connected set of atoms for each, neglecting the alternative orientation created by the mirror plane *m*' (Fig. 2) not contained in the molecule. The coordinates were input to the program POLYMOL. The resulting polyhedra created by the latter were subjected to reflection at plane *m*'. Figure 4 shows the result for the cation of compound **2**: The polyhedron is found to be almost superimposible to its reflected image.

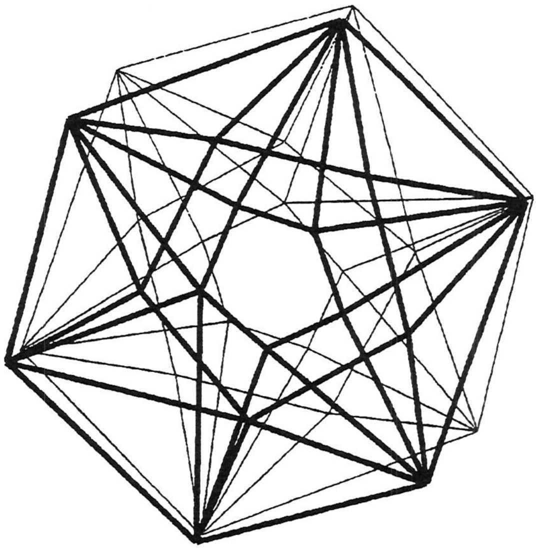

Fig. 4. Convex polyhedron enveloping the cation in 2; methyl groups were idealized as single spheric pseudo-atoms of van der Waals radius 1.95 Å

The situation is of course very similar for the almost isotypic cation in **1**. We conclude that the disorder is tolerated in these cases since it does not greatly affect space filling and intermolecular contacts.

Conclusion

In molecular structures showing disorder the alternative orientations of the molecules must respect reasonable distances to their nearest neighbors and will, at least roughly, fill the same part of the unit cell. As disorder is the exception to the rule, we do not expect every pseudosymmetric molecule to be disordered, but we do expect that molecules showing orientational or end-for-end disorder are pseudosymmetric. Therefore inspection of the molecular shape in the manner suggested here gives an indication whether a disorder affecting many atoms can be expected to occur. A certain degree of abstraction (in our case the convex polyhedron) will be necessary or at least helpful, since superimposed ball-and-stick models even of medium-sized molecules tend to show confusing complexity.

The model presented here is based on the assumption that molecules can be represented by convex enveloping polyhedra. Of the many limitations such an approach does imply at least two should be discussed here:

(a) A purely geometric interpretation in terms of faces, edges and vertices or of cup models does not consider charge distribution and specific intermolecular interactions such as hydrogen bonding.

(b) A convex polyhedron may be an inappropriate representation of a molecule, even in the purely geometric sense. A convex surface will of course not be suitable for modelling the shape of molecules with pronounced cavities in their enveloping surfaces.

With due care of these limitations, our model provides a simple and efficient tool for the representation of molecular shape and for the analysis of disorder problems related to molecular shape. In a forthcoming paper we shall show that it also can be used as a convenient tool for looking at the next neighbourhood of molecules or visualizing molecular packing in crystals.

Supplementary material

Tables with all atomic co-ordinates, thermal parameters, and interatomic distances (10 pages) are available from the authors. Structure factor tables and the above mentioned tables may also be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-XXXXXX, the names of the authors, and the journal citation.

The program POLYMOL is available in source code (written in language C for most parts within the confins of the ANSI Standard) and executable version (for IBM-PC) from the authors.

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