Monoclinic
$P2_1/n$
$a = 9.5188\ (1)$ Å
$b = 10.3406\ (1)$ Å
$c = 14.6223\ (2)$ Å
$\beta = 91.379\ (1)^\circ$
$V = 1438.86\ (3)$ Å^3
$Z = 4$
$D_x = 1.492$ Mg m^{-3}
D_m not measured

Cell parameters from 8192 reflections
$\theta = 2\text{–}28^\circ$
$\mu = 0.804$ mm^{-1}
$T = 293\ (2)$ K
Rectangular
0.4 × 0.3 × 0.1 mm
Yellow

Data collection

Siemens CCD diffractometer
ω scans
Absorption correction: empirical (Blessing, 1995)
$T_{\min} = 0.77$, $T_{\max} = 0.91$
28 024 measured reflections
3476 independent reflections

3034 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 28^\circ$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.088$
$S = 1.030$
3463 reflections
190 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.6378P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.299$ e Å^{-3}
$\Delta\rho_{\min} = -0.477$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection was carried out by a Siemens CCD X-ray diffractometer at 218 K. Data were collected by the double-pass method using the CCD area-detector system. The first 50 frames of data were recollected at the end of data collection to monitor crystal decay. H atoms were treated using appropriate riding models.

For both compounds, data collection: *SMART* (Siemens, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1997); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL-Plus*.

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References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Chen, S., Vasquez, L., Noll, B. C. & DuBois, M. R. (1997). *Organometallics*, **16**, 1757–1764.

Davies, S. G. & McCarthy, T. D. (1995). *Comprehensive Organometallic Chemistry* II, edited by E. W. Abel, F. G. A. Stone & G. Wilkinson, Vol. 12, pp. 1039–1070. Oxford: Elsevier Science Ltd.

Dickens, P. J., Slawin, A. M. Z., Widdowson, D. A. & Williams, D. J. (1989). *Tetrahedron Lett.* **29**, 103–106.

Heaton, S. B., Jones, G. B. & Pennington, W. T. (1993). *Acta Cryst.* C**49**, 1749–1753.

McLean, S., Trotz, U. O., Dichman, K. S., Fawcett, J. K. & Nyburg, S. C. (1970). *Tetrahedron Lett.* pp. 4561–4564.

Pigge, F. C., Fang, S. & Rath, N. P. (1998). *J. Organomet. Chem.* **559**, 131–140.

Semmelhack, M. F. (1995). *Comprehensive Organometallic Chemistry* II, edited by E. W. Abel, F. G. A. Stone & G. Wilkinson, Vol. 12, pp. 979–1038. Oxford: Elsevier Science Ltd.

Sheldrick, G. M. (1997*a*). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXS97. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1998). *SHELXTL-Plus.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1997). *SMART* and *SAINT. Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Solladie-Cavallo, A. (1985). *Polyhedron*, **4**, 901–927.

Sur, S., Ganesh, S., Pal, D., Puranik, V. G., Chakrabarti, P. & Sarkar, A. (1996). *J. Org. Chem.* **61**, 8362–8363.

Acta Cryst. (1998). C**54**, 1827-1830

A New Ni(dmit)$_2$ Salt with a Paramagnetic Cation: [Cu(bpy)$_3$][Ni(C$_3$S$_5$)$_2$]$_2$

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Abstract

The cation of the title compound, tris(2,2′-bipyridyl)-copper(II) bis[bis(2-thioxo-1,3-dithiole-4,5-dithiolato-S^4,S^5)nickelate(III)], [Cu(C$_{10}$H$_8$N$_2$)$_3$][Ni(C$_3$S$_5$)$_2$]$_2$, has crystallographic twofold rotation symmetry with all Cu—N distances almost equivalent in an octahedral environment. The NiS$_4$ coordination of the anion is significantly distorted from a square-planar geometry.

Comment

The synthesis of molecular conductors containing localized magnetic moments is a new challenge in the search for new properties (Cassoux, 1996). In the course of our work on conducting $M(dmit)_2$ systems ($dmit^{2-}$ is 2-thioxo-1,3-dithiole-4,5-dithiolato; M = Ni, Pd or Pt), one of the methods used to develop new molecular conductors has been the association of magnetic cations with $M(dmit)_2$-based anions. In such systems, interesting electrical properties may arise from the acceptor $M(dmit)_2$ part and magnetic properties from the cation. In the 1980s, Inoue and co-workers reported several Cu^{II} complexes combined with the organic acceptor tetracyanoquinodimethane (TCNQ) (Inoue & Inoue, 1980, 1981, 1983, 1984, 1985, 1986; Inoue *et al.*, 1982), some of which showed magnetic as well as conducting properties. Up to now, no partially oxidized $M(dmit)_2$ compounds with a paramagnetic transition metal complex as a counter-ion are known. Thus, we have been interested in combining some of the Cu^{II} complexes already used by Inoue and co-workers with the $M(dmit)_2$ systems, more specifically, $Cu(bpy)_2(NO_3)_2$ with $(NBu_4)[Ni(dmit)_2]$, where bpy is 2,2′-bipyridyl.

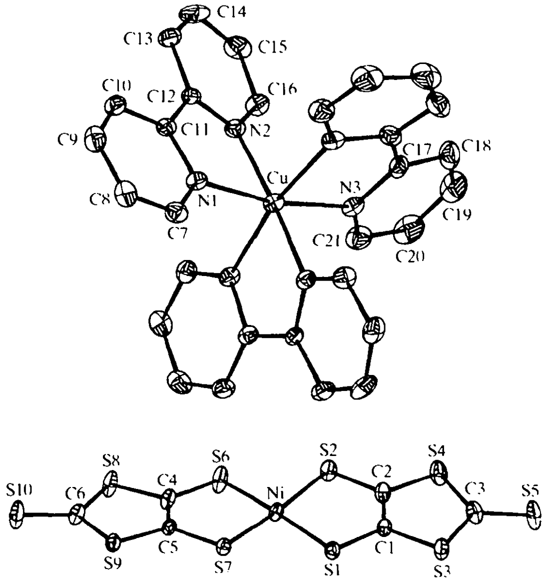
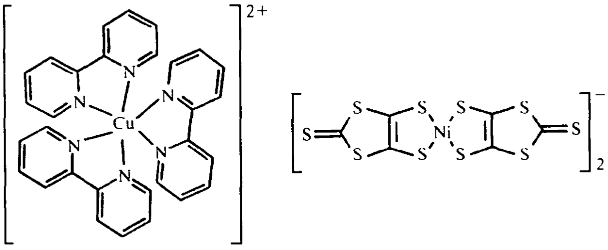


Fig. 1. The structure of the cation and anion of (I) showing the atomic labelling. Displacement ellipsoids are drawn at the 30% probability level and the H atoms of the bpy groups have been omitted for clarity.

The title structure, (I), consists of one crystallographically independent $Ni(dmit)_2$ unit and half a $Cu(bpy)_3$ unit (Fig. 1). The Cu atom lies on a twofold rotation axis. It should be noted that, unexpectedly, the cation has gained an extra bpy ligand upon its combination with the $[Ni(dmit)_2]^-$ anion. The stoichiometry of the compound is 1:2, but, as octahedral copper complexes show a Cu^{II} oxidation state, the $[Cu(bpy)_3]$ unit is a dication and, consequently, the $Ni(dmit)_2$ units bear a formal charge of -1.



(I)

Bond distances and angles (Table 1) within the $Ni(dmit)_2$ unit are in agreement with those found for other $[Ni(dmit)_2]^-$ complexes (Lindqvist *et al.*, 1982; Faulmann *et al.*, 1996). The most important feature is the non-planarity of the $Ni(dmit)_2$ unit; although each Ni(dmit) moiety is planar [maximum deviation 0.0735 (12) Å for S5], they are slightly twisted along the long axis of the molecule towards a tetrahedral geometry and form a dihedral angle of 10.19 (4)°.

The Cu—N distances are very similar, ranging from 2.065 (2) to 2.088 (2) Å, indicating the presence of a dynamic Jahn–Teller effect (Ham, 1962). This has also been found in the crystal structure of $[Cu(en)_3]SO_4$ (en is ethylenediamine; Cullen & Lingafelter, 1970). The mean Cu—N distance of 2.079 (2) Å is shorter than the mean Cu—N distances in $[Cu(en)_3]SO_4$ (Cullen & Lingafelter, 1970), $[Cu(bpy)_3](ClO_4)_2$ (Anderson, 1972) and $[Cu(phen)_3](ClO_4)_2$ (phen is 1,10-phenanthroline; Anderson, 1973) of 2.150, 2.133 and 2.134 Å, respectively. Short Cu—N distances of 2.095 (3) Å at 173 K were also found in the crystal structure of bis[tris(2-pyridyl)methane]copper(II) dinitrate, which also showed a dynamic Jahn–Teller effect (Astley *et al.*, 1995).

Contrary to what is found in partially oxidized $Ni(dmit)_2$ compounds, no separated two-dimensional layers of anions and cations are found in the structural arrangement of $[Cu(bpy)_3][Ni(dmit)_2]_2$. The $Ni(dmit)_2$ units are rotated 94.65 (1)° towards each other and the $Cu(bpy)_3$ units are positioned in the cavities between. Fig. 2 shows the complex network of short S⋯S interactions (dotted lines) between adjacent molecules of the $Ni(dmit)_2$ units. Most of these interactions (Fig. 2*a* and Table 2) take place between two $Ni(dmit)_2$ units in which the Ni atoms are separated by 6.2279 (9) Å (symmetry code: $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$). These units form a pair (A/A') which shows two S⋯S interactions [3.4032 (13) and 3.6705 (13) Å] with two other pairs (B/B' and C/C'), with the mean planes of these latter pairs above and below the plane of the middle pair (Fig. 2*b*). Consequently, a stairway of $Ni(dmit)_2$ pairs is formed in the [110] direction. Due to the 94.65 (1)° rotation of the $Ni(dmit)_2$ units, an equivalent stairway of such couples also exists in a perpendicular direction, *i.e.* $[1\bar{1}0]$ (Fig. 2*c*). The angle between the mean plane of the $Ni(dmit)_2$ units of these two directions is 35.91 (2)°. The

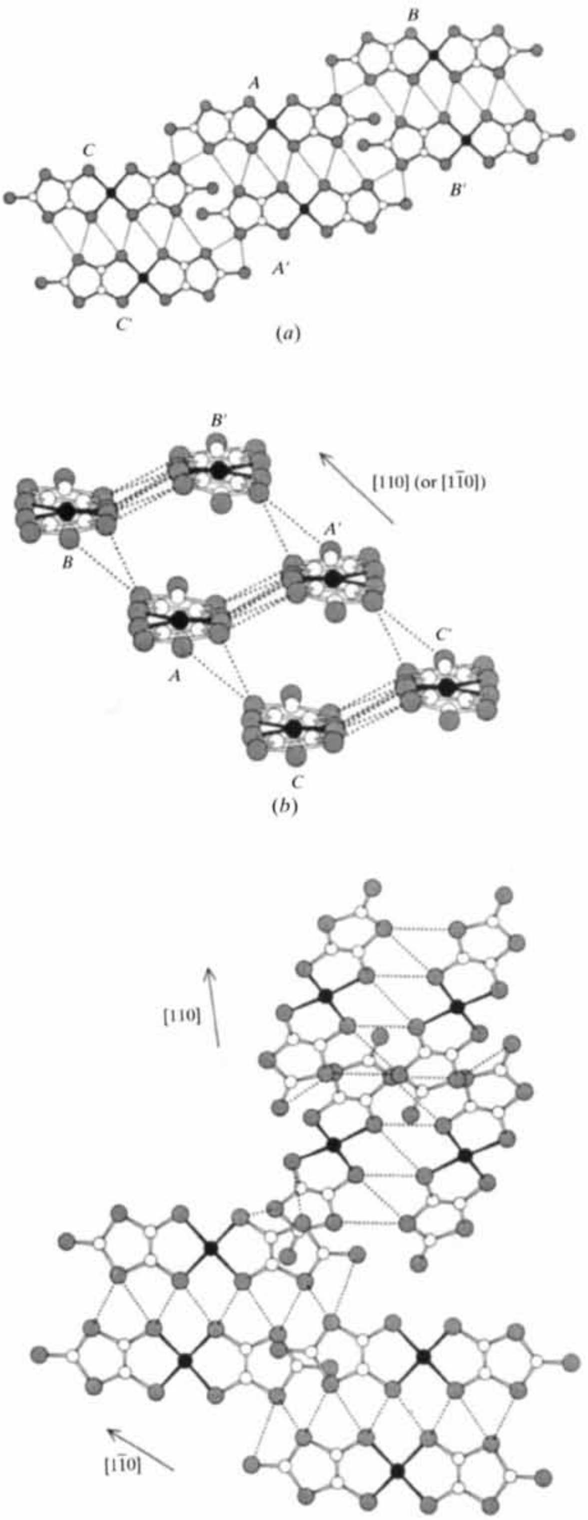


Fig. 2. Intermolecular S$\cdots$S contacts (dotted lines) in (I): (*a*) view of the Ni(dmit)$_2$ units perpendicular to the Ni—S1—S2 plane, (*b*) view of the Ni(dmit)$_2$ units along their long axis and (*c*) view of the two different kinds of Ni(dmit)$_2$ stairway.

two types of stairway (Fig. 2*c*) are connected through a short S$\cdots$S interaction [3.4657 (11) Å]. Every pair of Ni(dmit)$_2$ units is then connected through short S$\cdots$S interactions to four other pairs.

Experimental

The synthesis of $Cu(bpy)_2(NO_3)_2\cdot H_2O$ was carried out by slow addition of pure 2,2′-bipyridyl (2 mmol) to an ethanol solution (10 ml) of $Cu(NO_3)_2\cdot 2.5H_2O$, followed by filtration and drying in air. Analysis calculated for $C_{20}H_{18}CuN_6O_7$: C 46.38, H 3.50, N 16.23%; found: C 46.40, H 3.02, N 16.42%. $(NBu_4)[Ni(dmit)_2]$ was synthesized according to the literature method of Lindqvist *et al.* (1982). $[Cu(bpy)_3][Ni(dmit)_2]_2$ was synthesized by slow diffusion of solutions of $Cu(bpy)_2(NO_3)_2\cdot H_2O$ and $(NBu_4)[Ni(dmit)_2]$ in a three-compartment cell under an N_2 atmosphere. The compartments of the cell were separated by a fine porosity glass frit. One of the outer compartments was filled with a 2 m*M* solution of $(NBu_4)[Ni(dmit)_2]$ in acetone and the other outer compartment with a 10 m*M* solution of $[Cu(bpy)_2](NO_3)_2\cdot H_2O$ in methanol. The middle compartment was filled with a 1:1 mixture of methanol and acetone. Crystals were obtained in this latter compartment after a few weeks.

Crystal data

$[Cu(C_{10}H_8N_2)_3][Ni(C_3S_5)_2]_2$
$M_r = 1434.84$
Monoclinic
$C2/c$
$a = 17.066$ (2) Å
$b = 16.863$ (2) Å
$c = 18.487$ (2) Å
$\beta = 94.650$ (11)°
$V = 5302.8$ (11) Å^3
$Z = 4$
$D_x = 1.797$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5000 reflections
$\theta = 1.97–24.22°$
$\mu = 1.929$ mm^{-1}
$T = 160$ (2) K
Rectangular plate
0.40 × 0.25 × 0.03 mm
Dark brown

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1996*c*)
$T_{min} = 0.564$, $T_{max} = 0.923$
16 997 measured reflections
4212 independent reflections

3421 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 24.22°$
$h = -19 \rightarrow 19$
$k = -19 \rightarrow 19$
$l = -20 \rightarrow 21$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.070$
$S = 1.003$
4212 reflections
321 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0420P)^2 + 1.3451P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.445$ e Å^{-3}
$\Delta\rho_{min} = -0.596$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni—S6	2.1517 (9)	S7—C5	1.721 (3)
Ni—S1	2.1602 (8)	S8—C6	1.731 (3)
Ni—S7	2.1628 (8)	S8—C4	1.749 (3)
Ni—S2	2.1651 (8)	S9—C6	1.727 (3)
S1—C1	1.718 (3)	S9—C5	1.746 (3)
S2—C2	1.714 (3)	S10—C6	1.652 (3)
S3—C1	1.739 (3)	C1—C2	1.360 (4)
S3—C3	1.740 (3)	C4—C5	1.352 (4)
S4—C3	1.733 (3)	Cu—N1	2.065 (2)
S4—C2	1.750 (3)	Cu—N2	2.083 (2)
S5—C3	1.640 (3)	Cu—N3	2.088 (2)
S6—C4	1.719 (3)		
S6—Ni—S1	174.37 (4)	N1—Cu—N2$^{\rm i}$	98.42 (9)
S6—Ni—S7	93.14 (3)	N2—Cu—N2$^{\rm i}$	175.72 (13)
S1—Ni—S7	87.14 (3)	N1—Cu—N3$^{\rm i}$	94.07 (9)
S6—Ni—S2	87.43 (3)	N2—Cu—N3$^{\rm i}$	90.63 (9)
S1—Ni—S2	92.93 (3)	N1—Cu—N3	168.92 (9)
S7—Ni—S2	173.52 (4)	N2—Cu—N3	92.67 (9)
N1—Cu—N1$^{\rm i}$	93.97 (13)	N3$^{\rm i}$—Cu—N3	79.06 (14)
N1—Cu—N2	78.62 (9)		

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

Table 2. *Intermolecular S···S contacts (Å) shorter than 3.70 Å*

S2···S2$^{\rm i}$	3.3959 (15)	S4···S6$^{\rm i}$	3.3904 (12)
S2···S6$^{\rm i}$	3.4936 (11)	S4···S8$^{\rm i}$	3.6581 (11)
S3···S8$^{\rm ii}$	3.4032 (13)	S7···S9$^{\rm iii}$	3.4657 (11)
S3···S10$^{\rm ii}$	3.6705 (13)		

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (ii) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (iii) $-x, y, \frac{1}{2}-z$.

H atoms were placed geometrically at a distance of 0.95 Å from and riding on their adjacent C atom, with an isotropic displacement parameter 20% higher than that of the parent atom. Although it would have been experimentally possible to locate the area detector 70 mm from the crystal (this would have allowed measurement up to $\theta_{\max} = 26.2°$), it was deliberately placed 80 mm from the crystal ($\theta_{\max} = 24.2°$). The reasons for this are: (i) a previous data collection on a four-circle diffractometer had shown that no significant diffraction occurred above 21°, showing that the diffracting power of the crystal was low, and (ii) because of this poor diffracting power, recorded reflections are mainly concentrated in the central part of the area detector. Overlapping reflections that may have occurred at a distance of 70 mm would have been eliminated during the integration process. This may have led to a low reflection-to-parameter ratio.

Data collection: *IPDS Software* (Stoe & Cie, 1996*a*). Cell refinement: *IPDS Software*. Data reduction: *X-RED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *CAMERON* (Watkin *et al.*, 1996). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1205). Services for accessing these data are described at the back of the journal.

References

Anderson, O. P. (1972). *J. Chem. Soc. Dalton Trans.* pp. 2597–2601.

Anderson, O. P. (1973). *J. Chem. Soc. Dalton Trans.* pp. 1237–1241.

Astley, T., Ellis, P. J., Freeman, H. C., Hitchman, M. A., Keene, F. R. & Tiekink, E. R. T. (1995). *J. Chem. Soc. Dalton Trans.* pp. 595–601.

Cassoux, P. (1996). *Science*, **272**, 1277–1278.

Cullen, D. L. & Lingafelter, E. C. (1970). *Inorg. Chem.* **9**, 1858–1864.

Faulmann, C., Errami, A., Donnadieu, B., Malfant, I., Legros, J.-P., Cassoux, P., Rovira, M. & Canadell, E. (1996). *Inorg. Chem.* **35**, 3856–3873.

Ham, N. S. (1962). *Spectrochim. Acta*, **18**, 775–789.

Inoue, M. & Inoue, M. B. (1980). *Inorg. Chim. Acta*, **45**, L129–130.

Inoue, M. & Inoue, M. B. (1983). *Mol. Cryst. Liq. Cryst.* **95**, 183–189.

Inoue, M. & Inoue, M. B. (1984). *J. Chem. Soc. Chem. Commun.* pp. 790–791.

Inoue, M. & Inoue, M. B. (1985). *J. Chem. Soc. Faraday Trans.* **81**, 539–547.

Inoue, M. & Inoue, M. B. (1986). *Inorg. Chem.* **25**, 37–41.

Inoue, M., Inoue, M. B., Seto, T. & Nakamura, D. (1982). *Mol. Cryst. Liq. Cryst.* **86**, 139–146.

Inoue, M. B. & Inoue, M. (1981). *Chem. Phys. Lett.* **80**, 585–588.

Lindqvist, O., Andersen, L., Sieler, J., Steimecke, G. & Hoyer, E. (1982). *Acta Chem. Scand. Ser. A*, **36**, 855–856.

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

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Stoe & Cie (1996*a*). *IPDS Software.* Version 2.86. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1996*b*). *X-RED. Data Reduction Program.* Version 1.08. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1996*c*). *X-SHAPE. Crystal Optimization for Numerical Absorption Correction.* Version 1.01. Stoe & Cie, Darmstadt, Germany.

Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON.* Chemical Crystallography Laboratory, University of Oxford, England.

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Redetermination of the Germanium Dichloride Complex with 1,4-Dioxane at 173 K

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Abstract

The structure of germanium dichloride–1,4-dioxane (1/1), $GeCl_2.C_4H_8O_2$, (1), has been redetermined at 173 K and refined in space group *C*2/*c*, rather than *Cc* which was used in the original determination by Kulishov *et al.* [*Zh. Strukt. Khim.* (1970), **11**, 61–64]. The data from the original determination have already been used to redetermine the structure of (1) in the revised space group *C*2/*c* [Marsh (1997). *Acta Cryst.*