Table 2. *I···I and S···I contact distances (Å)*

$I7\cdots I1^{i}$	4.106 (2)	$I3\cdots I6^{vi}$	3.776 (2)
$I6\cdots I3^{ii}$	3.776 (2)	$I5\cdots I7$	3.336 (2)
$I3\cdots I3^{iii}$	3.871 (2)	$S5\cdots I2^{ii}$	3.913 (4)
$I1\cdots I7^{iv}$	4.106 (2)	$S13\cdots I2$	3.892 (4)
$I5\cdots I7^{v}$	4.133 (2)		

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

H atoms were included at geometrically calculated positions 0.98 Å from their parent C atoms, and during refinement were constrained to ride on these with $U_{iso}(H) = 1.2U_{eq}(C)$. The highest difference electron-density peak lay 0.99 Å from I2, while the deepest trough was located 0.74 Å from I6; these therefore possess no chemical significance.

Data collection: *STADI*4 (Stoe & Cie, 1995*a*). Cell refinement: *STADI*4. Data reduction: *X-RED* (Stoe & Cie, 1995*b*). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL*96.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1058). Services for accessing these data are described at the back of the journal.

References

Blake, A. J., Devillanova, F. A., Gould, R. O., Li, W.-S., Lippolis, V., Parsons, S., Radek, C. & Schröder, M. (1998). *Chem. Soc. Rev.* **27**, 195–205.

Blake, A. J., Gould, R. O., Li, W.-S., Lippolis, V., Parsons, S., Radek, C. & Schröder, M. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 293–296.

Blake, A. J., Gould, R. O., Parsons, S., Radek, C. & Schröder, M. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2374–2376.

Blake, A. J., Li, W.-S., Lippolis, V., Parsons, S. & Schröder, M. (1998). *Acta Cryst.* **C54**, 1408–1410.

Blake, A. J., Li, W.-S., Lippolis, V. & Schröder, M. (1998). *Acta Cryst.* **C54**, 299–302.

Blake, A. J., Lippolis, V., Parsons, S. & Schröder, M. (1996). *J. Chem. Soc. Chem. Commun.* pp. 2207–2208.

Blake, A. J., Lippolis, V., Parsons, S. & Schröder, M. (1998). *Acta Cryst.* **C54**, 293–295.

Blake, A. J. & Schröder, M. (1990). *Adv. Inorg. Chem.* **35**, 1–80.

Deplano, P., Devillanova, F. A., Ferraro, J. R., Isaia, F., Lippolis, V. & Mercuri, M. L. (1992). *Appl. Spectrosc.* **46**, 1625–1629.

Farrugia, L. J., Norman, N. C. & Pickett, N. L. (1998). *Acta Cryst.* **C54**, 476–479.

Jircitano, A. J., Colton, M. C. & Bowman Mertes, K. (1981). *Inorg. Chem.* **20**, 890–896.

Menon, S. & Rajasekharan, M. V. (1997). *Inorg. Chem.* **36**, 4983–4987.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1996). *SHELXL96. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Stoe & Cie (1995*a*). *STADI4. Diffractometer Control Program for Windows*. Version 1.06a. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1995*b*). *X-RED. Data Reduction Program for Windows*. Version 1.08. Stoe & Cie, Darmstadt, Germany.

Tebbe, K.-F. & Buchem, R. (1997). *Angew. Chem. Int. Ed. Engl.* **36**, 1345–1346.

Acta Cryst. (1998). C**54**, 1413–1416

Ferrocene, Ferrocenium and a Bis(maleonitriledithiolate) Complex of Nickel

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Abstract

The crystal structure of the title compound, diferrocenium bis{bis[1,2-dimercaptoethene-1,2-dicarbonitrilato(2−)-*S*,*S*′]nickel(III)} ferrocene, is a 2:3 complex of $[Ni\{C_2S_2(CN)_2\}_2]$ and $[Fe(C_5H_5)_2]$. The structural data suggest that the formula for this compound can be written as $[Fe(C_5H_5)_2]_2[Ni\{C_2S_2(CN)_2\}_2]_2.[Fe(C_5H_5)_2]$.

Comment

Organometallic charge-transfer complexes have attracted attention in recent years, since some of them exhibit interesting electronic or magnetic properties (Green *et al.*, 1988). The $[M(mnt)_2]^{n-}$ anions $\{M$ = Ni, Pd or Pt; mnt = maleonitriledithiolate, *i.e.* $[C_2S_2(CN)_2]^{2-}\}$ have a delocalized π-electron system, and their redox potentials vary depending on the metal. They are considered electron acceptors and have formed quasi-one-dimensional conductors, such as $Li_{0.75}[Pt(mnt)_2].2H_2O$ (Underhill & Armad, 1981). On the other hand, ferrocene and alkyl-substituted ferrocenes may be regarded as interesting electron donors and can form charge-transfer salts with various electron acceptors. Some such salts are mixed-valence systems, with segregated stacks of donors and acceptors, giving rise to conducting solids such as $[Fe(\eta\text{-}C_5H_4Me)_2](TCNQ)_2$ (Wilson *et al.*, 1979), where TCNQ is tetracyanoquinodimethane. Other crystals may consist of mixed stacks of alternating $D^+A^-D^+A^-$ (D = donor and A = acceptor), resulting in insulators which may exhibit interesting cooperative magnetic phenomena; an example is the ferromagnetic salt $[Fe(\eta\text{-}C_5Me_5)_2](TCNE)$

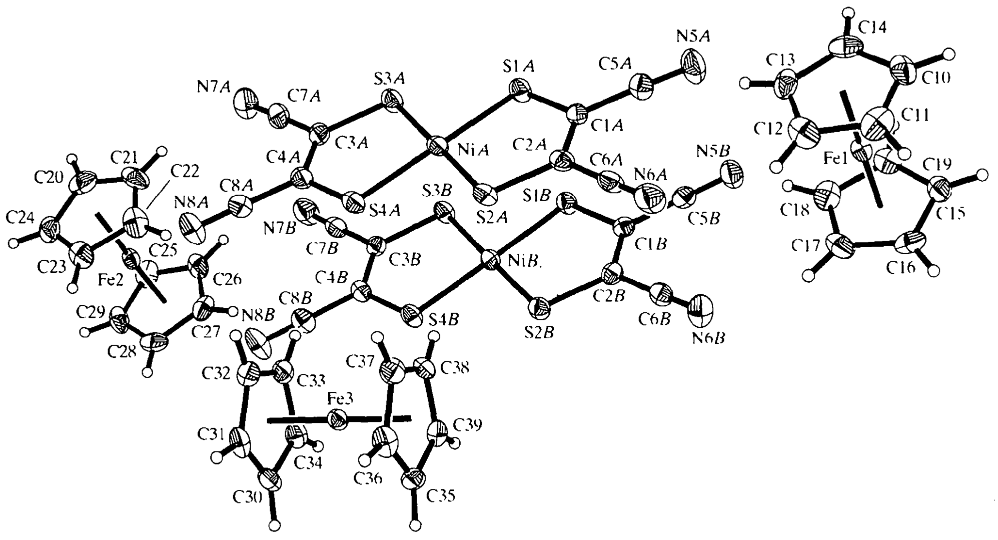
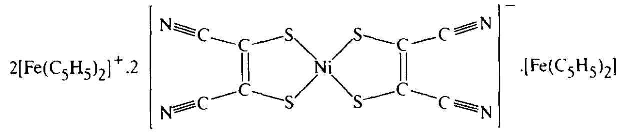


Fig. 1. A labeled view of the title compound, (I), showing 50% probability ellipsoids.

(Miller *et al.*, 1986), where TCNE is tetracyanoethylene. We have synthesized the title compound, $2[Fe(C_5H_5)_2]^+.2[Ni\{C_2S_2(CN)_2\}_2]^-.[Fe(C_5H_5)_2]$, (I).



(I)

A drawing of the asymmetric unit of (I) is shown in Fig. 1. The Ni complex is composed of two maleonitriledithiolate ligands chelating an Ni atom, with the four S atoms forming a square plane around the Ni atom. The Ni atom is displaced from the plane of the S atoms by only 0.006 (1) Å, on average. The mean Ni—S distance is 2.1490 (11) Å, and the mean C≡N bond length is 1.143 (4) Å. These values are consistent with the corresponding values in $[Ni(mnt)_2]^-$, but are quite different from those in $[Ni(mnt)_2]^{2-}$ (McCleverty, 1968).

The crystal packing is shown in Fig. 2. The $[Ni(mnt)_2]^-$ anions form discrete stacks of four. These stacks of four are two pairs, related by a center of symmetry. The Ni atoms of each pair are separated by 3.539 (1) Å, and the pairs themselves are separated by 3.802 (1) Å. Associated with each pair is a ferrocene (containing Fe3), and each stack has a ferrocenium at either end. That the former $[Fe(C_5H_5)_2]$ is ferrocene and not ferrocenium is suggested by the observation that the Fe3–centroid distance and the Fe3—C distances are approximately 0.05 Å shorter than the corresponding distances in the other two $[Fe(C_5H_5)_2]$ moieties, containing Fe1 and Fe2. The Fe—C distances for Fe1 and Fe2 range between 2.070 (4) and 2.094 (4) Å, averaging 2.081 (6) Å. The corresponding values for Fe3 are 2.031 (3)–2.042 (4) Å, with a mean of 2.036 (3) Å. This is consistent with the corresponding distances in both ferrocene (Dunitz *et al.*, 1956) and ferrocenium

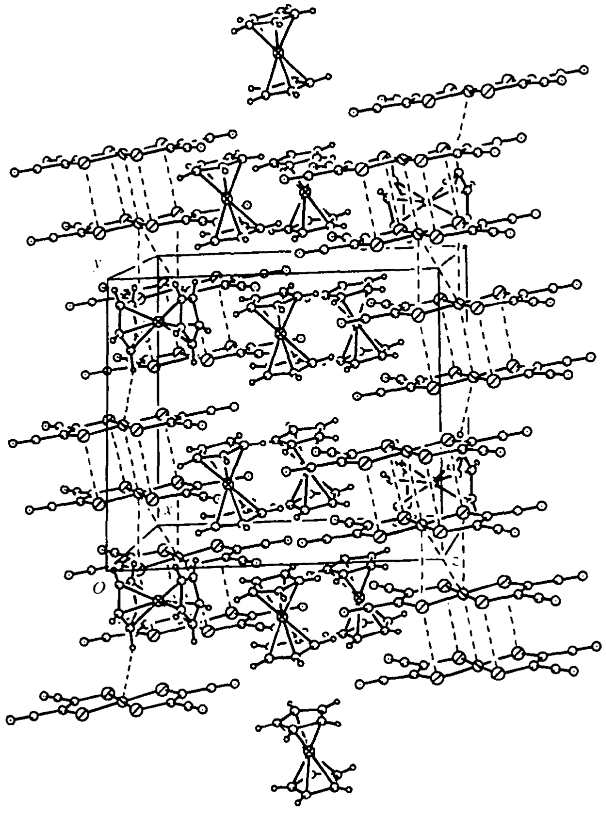


Fig. 2. A packing diagram of (I).

(Mammano *et al.*, 1977). The other two $[Fe(C_5H_5)_2]$ moieties, containing Fe1 and Fe2, pack end-to-end in columns of four, which are parallel to and overlapping with the stacks of $[Ni(mnt)_2]^-$ anions. The ferrocenium columns also overlap each other.

In light of the above discussion on the assignment of charges, the formula for the title compound is best written as $2[Fe(C_5H_5)_2]^+.2[Ni\{C_2S_2(CN)_2\}_2]^-.[Fe(C_5H_5)_2]$.

Experimental

The title compound was synthesized by the reaction between $[Fe(\eta\text{-}C_5H_5)_2]Cl$ and $Na_2[Ni(mnt)_2]$. To a solution of $Na_2(mnt)$ (0.93 g, 5 mmol; Davidson & Holm, 1967) in a mixture of water (10 ml) and ethanol (10 ml) was added an aqueous saturated solution of $NiCl_2.6H_2O$ (0.6 g, 2.5 mmol), resulting in a deep-red solution. Then an aqueous solution of $[Fe(\eta\text{-}C_5H_5)_2]Cl$ {20 ml, previously prepared from 10 mmol $[Fe(\eta\text{-}C_5H_5)_2]$ (McCleverty, 1968)} was added. The mixture was allowed to stand overnight at room temperature. The resulting black precipitate was filtered, washed with water, ethanol and diethyl ether, and dried in air (460 mg, 35% yield based on $NiCl_2$). Single crystals suitable for X-ray diffraction studies were obtained by recrystallization from a solution in acetonitrile.

Crystal data

$[Fe(C_5H_5)_2]_2[Ni(C_4N_2S_2)_2]_2.[Fe(C_5H_5)_2]$
$M_r = 1236.23$
Triclinic
$P\bar{1}$
$a = 12.030\,(2)$ Å
$b = 13.652\,(3)$ Å
$c = 15.462\,(3)$ Å
$\alpha = 87.91\,(3)°$
$\beta = 77.62\,(3)°$
$\gamma = 72.56\,(3)°$
$V = 2365.3\,(8)$ Å^3
$Z = 2$
$D_x = 1.736$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.5\text{–}15.3°$
$\mu = 2.08$ mm^{-1}
$T = 160$ K
Needle
0.29 × 0.26 × 0.14 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.67$, $T_{\max} = 0.75$
17 416 measured reflections
8310 independent reflections

6820 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 25°$
$h = -12 \rightarrow 14$
$k = -15 \rightarrow 16$
$l = -17 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.064$
$S = 1.50$
8300 reflections
724 parameters
All H atoms refined
$w = 1/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\max} = -0.002$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni*A*—S4*A*	2.1482 (11)	Ni*B*—S1*B*	2.1451 (11)
Ni*A*—S2*A*	2.1498 (11)	Ni*B*—S4*B*	2.1466 (11)
Ni*A*—S3*A*	2.1503 (11)	Ni*B*—S3*B*	2.1474 (10)
Ni*A*—S1*A*	2.1537 (11)	Ni*B*—S2*B*	2.1510 (10)
S1*A*—C1*A*	1.714 (3)	S1*B*—C1*B*	1.714 (3)
S2*A*—C2*A*	1.706 (3)	S2*B*—C2*B*	1.715 (3)
S3*A*—C3*A*	1.718 (3)	S3*B*—C3*B*	1.704 (3)
S4*A*—C4*A*	1.717 (3)	S4*B*—C4*B*	1.715 (3)
N5*A*—C5*A*	1.140 (4)	N5*B*—C5*B*	1.143 (4)
N6*A*—C6*A*	1.140 (4)	N6*B*—C6*B*	1.147 (4)
N7*A*—C7*A*	1.149 (4)	N7*B*—C7*B*	1.145 (4)
N8*A*—C8*A*	1.139 (4)	N8*B*—C8*B*	1.143 (4)
S4*A*—Ni*A*—S2*A*	86.64 (4)	S4*B*—Ni*B*—S3*B*	92.72 (4)
S4*A*—Ni*A*—S3*A*	92.77 (4)	S1*B*—Ni*B*—S2*B*	92.73 (4)
S2*A*—Ni*A*—S3*A*	179.34 (4)	S4*B*—Ni*B*—S2*B*	87.70 (4)
S4*A*—Ni*A*—S1*A*	179.35 (4)	S3*B*—Ni*B*—S2*B*	179.19 (4)
S2*A*—Ni*A*—S1*A*	92.71 (4)	N5*B*—C5*B*—C1*B*	179.6 (4)
S3*A*—Ni*A*—S1*A*	87.87 (4)	N6*B*—C6*B*—C2*B*	178.4 (4)
N5*A*—C5*A*—C1*A*	177.5 (4)	N7*B*—C7*B*—C3*B*	178.4 (4)
N7*A*—C7*A*—C3*A*	178.2 (4)	N8*B*—C8*B*—C4*B*	179.0 (4)
N6*A*—C6*A*—C2*A*	178.9 (4)	S1*A*—Ni*A*—Ni*B*	88.96 (4)
N8*A*—C8*A*—C4*A*	178.4 (4)	S2*A*—Ni*A*—Ni*B*	91.52 (4)
S1*B*—Ni*B*—S4*B*	179.49 (4)	S3*A*—Ni*A*—Ni*B*	88.19 (4)
S1*B*—Ni*B*—S3*B*	86.85 (4)	S4*A*—Ni*A*—Ni*B*	90.93 (4)

The intensities were collected at 160 K and averaged in point group $\bar{1}$. The variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$, and the variances of the merged data were obtained by propagation of error plus the addition of another term, $(0.014\langle I\rangle)^2$. The structure was solved by direct methods. The initial solution contained the positions of all the non-H atoms. After three cycles of least-squares refinement, the H atoms were revealed as the 30 strongest features of the difference Fourier map. All H atoms were refined freely. The 30 C—H distances range between 0.78 (4) and 1.00 (4) Å, with an average of 0.91 (4) Å. The H-atom U values lie between 0.018 (9) and 0.05 (1) Å^2, with a mean of 0.03 (1) Å^2. Refinement was carried out on F^2 for all reflections, except for ten with very negative F^2.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CRYM* (Duchamp, 1964). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1370). Services for accessing these data are described at the back of the journal.

References

Davidson, A. & Holm, R. H. (1967). *Inorganic Synthesis*, Vol. 10, edited by E. L. Meutterties, pp. 8–26. New York: McGraw-Hill.

Duchamp, D. J. (1964). *Am. Crystallogr. Assoc. Meet.*, Bozeman, Montana, USA, pp. 29–30, Paper B14.

Dunitz, J. D., Orgel, L. E. & Rich, A. (1956). *Acta Cryst.* **9**, 373–375.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Green, M. L. H., Qin, J. & O'Hare, D. (1988). *J. Organomet. Chem.* **358**, 375–387.
McCleverty, J. A. (1968). *Prog. Inorg. Chem.* **10**, 49–221.
Mammano, N. J., Zalkin, A., Landers, A. & Rheingold, A. L. (1977). *Inorg. Chem.* **16**, 297–300.
Miller, J. S., Calabrese, J. C., Epstein, A. J., Bigelow, R. W., Zhang, J. H. & Reiff, W. M. (1986). *J. Chem. Soc. Chem. Commun.* pp. 1026–1028.
North, A. C. T. , Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for Refinement of Crystal Structures.* University of Göttingen, Germany.
Underhill, A. E. & Armad, M. M. (1981). *J. Chem. Soc. Chem. Commun.* pp. 67–68.
Wilson, S. R., Corvan, P. J., Seider, R. P., Hodgson, D. J., Brookhart, M., Hatfield, W. E., Miller, J. S., Reis, A. H. Jr, Rogan, P. K., Gebert, E. & Epstein, A. J. (1979). *Molecular Metals*, edited by W. E. Hartfield, pp. 407–414. New York: Plenum Press.

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catena-Poly[[(2,3-benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene-κ^5O)-potassium]-μ-(picrato-O^1,O^2:O^5)]

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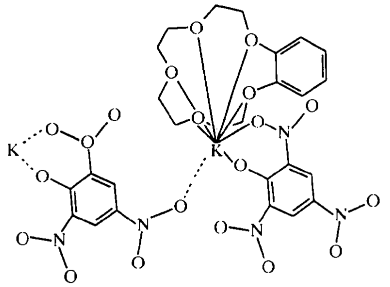
Abstract

The title compound, $[K(C_6H_2N_3O_7)(C_{14}H_{20}O_5)]_n$, or [K(B15C5)Pic], where Pic is picrate, was synthesized and its crystal structure shown to be an infinite linear-chain polymer with the K(B15C5) moieties bridged by the picrate groups. The K^+ ion is surrounded by eight O atoms in a distorted triangular dodecahedral arrangement. The macrocycle ligand bonds to K^+ using all five O atoms [K—O 2.760 (2)–2.970 (2) Å]. The K^+ ion is bonded to the bridging picrate anion *via* a nitro and the phenolic O atom [K—O 2.808 (2) and 2.871 (2) Å, respectively], and also *via* another nitro O atom of an adjacent symmetry-related picrate anion [K—O 3.060 (2) Å].

Comment

Benzo-15-crown-5 [B15C5] is well known to form 1:2 (metal–ligand) complexes with potassium salts because the K^+ ion is too large to fit into the cavity of the 15-membered ring. Crystal structure analyses of such compounds have revealed that the K^+ ion is ten-coordinate, being 'sandwiched' between two crowns and with no interaction with the counter-anion (Mallinson & Truter, 1972; Bhagwat *et al.*, 1981; Weber & Czugler, 1982; Sheldrick & Poonia, 1986; Mao *et al.*, 1993). We now report the synthesis and crystal structure of a novel 1:1 complex of potassium picrate with benzo-15-crown-5, [K(B15C5)Pic], where Pic is picrate.



[K(B15C5)Pic]

A view of [K(B15C5)Pic] showing the K^+ coordination is given in Fig. 1. In the crystal, there is an infinite linear-chain polymer extending along the *b*-axis direction, with K(B15C5) moieties bridged by picrate anions in a head-to-tail manner to form $[K(B15C5)Pic]_\infty$ chains. We are not aware of any similar polymer in metal–crown ether complex chemistry.

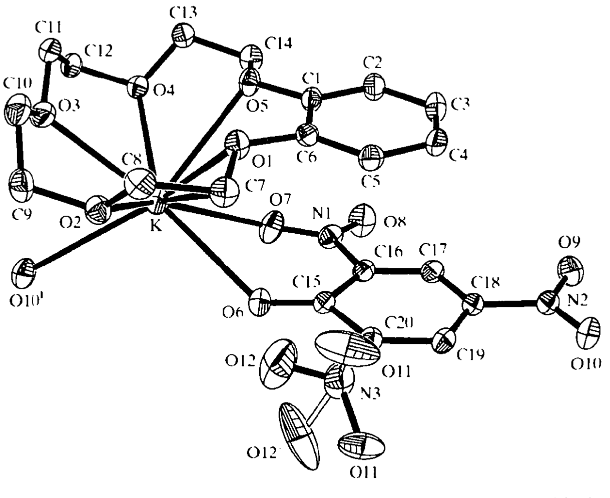


Fig. 1. A view of the asymmetric unit of the title compound with the two orientations of the disordered nitro group shown. Anisotropic displacement ellipsoids are drawn at the 30% probability level. H atoms are not shown and the symmetry code is as in Table 1.

Fig. 2 shows part of the extended chain structure in which the K^+ cation is involved in ion–dipole interactions to the five O atoms of the 15-membered ring and two interactions with a chelate picrate anion,