Inorganica Chimica Acta, 111 (1986) L43–L47

[Nickel(II)(trithianonane)(picrate)(H_2O)] (picrate); a Complex with a Chelating Picrate Group

JUDITH ANN R. HARTMAN and STEPHEN R. COOPER*

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K. and Department of Chemistry, Harvard University, Cambridge, Mass. 02138, U.S.A.

Received August 7, 1985

Picrate is generally considered as a non-coordinating anion, in effect the organic equivalent of perchlorate. Few examples of picrate coordination have been structurally characterized, one of the few examples being μ-pyrrolyl(picrate)bis(tricarbonylmanganese) dimer [1]. In the course of our investigation of the Ni(II)hexathia-18-crown-6 and Ni(II)bis(trithianone) complexes we isolated [Ni(II)(trithianonane)(picrate)(H_2O)] (picrate), a complex that structural investigation shows to contain a chelating picrate anion. We report herein the results of that study.

Experimental

Preparation of Compounds

Trithianonane was prepared by reaction of trithiaheptane and methyl iodide [2]. Nickel(II) picrate was prepared from nickel(II) carbonate and picric acid, then dried *in vacuo* over phosphorous pentoxide. **Caution**: although this compound does not appear to be particularly sensitive to shock or heat, it, like all picrates, should be prepared only in small quantities and handled carefully. Nitromethane was distilled from phosphorous pentoxide and stored over activated molecular sieves. All other chemicals were used as received.

[Ni(trithianonane)(picrate)(H_2O)] (picrate)

Nickel(II) picrate (70 mg, 0.136 mmol) was dissolved in 5 ml of warm (35 °C) 20% acetic anhydride in nitromethane. Trithianonane (200 mg, 1.1 mmol) was added and the dark brown solution was allowed to concentrate slowly by evaporation. The resulting long dark brown prisms were collected by filtration to give crystals suitable for X-ray diffraction studies. IR (KBr, nujol): 3320(m,vbr), 3200(m,vbr), 1756(w), 1622(sh), 1616(s), 1600(sh), 1578(m), 1567(m), 1560(sh), 1550(sh), 1545(m), 1540(sh), 1520(m), 1490(m), 1465(m,br), 1415(m), 1376(m), 1365(m), 1350(sh), 1328(m), 1315(w), 1300(sh), 1260(m), 1250(m), 1162(m), 1092(m), 1085(m), 1028(w), 980(w), 972(sh), 945(w), 932(sh), 925(m), 910(w), 858(w), 841(w), 830(w), 822(vw), 790(w), 786(m), 750(sh), 742(m), 720(m), 715(sh), 655(w), 541(w).

X-ray Diffraction Data Collection

A dark brown parallel-piped crystal of [Ni(trithianonane)(picrate)(H_2O)] (picrate) (0.25 × 0.20 × 0.45 mm) mounted in a glass capillary was centered on a Syntex R3 diffractometer. Fifteen reflections chosen from a rotation photograph were indexed to give a primitive monoclinic unit cell. The systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) uniquely indicated the space group to be $P2_1/n$. Accurate cell dimensions and orientation matrix were determined by least-squares refinement on 12 sets of Friedel pairs with $25° < 2\theta < 30°$. A summary of crystallographic details is presented in Table I. Three reflections (0 0 18, 0 2 0, 8 0 0) were checked every 123 reflections as orientation and intensity

TABLE I. Crystallographic Data for [Ni(trithianonane)(picrate)(H_2O)] picrate

M_r	715.32
Space group	$P2_1/n$
a (Å)	12.118(3)
b (Å)	9.369(3)
c (Å)	26.283(8)
α (°)	90
β (°)	98.47(2)
γ (°)	90
V (Å^3)	2951.47
D_c (g cm^{-3})	1.61
Z	4
λ	Mo Kα
$F(000)$	1591.69
μ (cm^{-1})	9.49
Crystal dimensions (mm)	0.25 × 0.20 × 0.45
Reflections collected	$+h$, $+k$, $\pm l$
Number of reflections collected	5224
Unique data with $F^2 > 2\sigma(F^2)$	3055
2θ range (°)	3–48
Final R (%)	5.79
Final R_w (%)	6.15
G.O.F.[a]	1.182
Number of variables	406
T	ambient
Scan rate	2.00–29.3
Mode	θ - 2θ
Maximum transmission factor	0.678
Minimum transmission factor	0.593
R_{merg}	0.0174

[a] The goodness of fit is defined as $[w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the number of data and variables, respectively.

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

standards; no decomposition was noted. The data were corrected for Lorentz and polarization effects and an empirical absorption correction was carried out with the program XEMP. Atomic scattering factors, including anomalous dispersion, were taken from the International Tables of X-ray Crystallography [3]. Crystallographic calculations were performed on a Nova 3 minicomputer with the Nicolet SHELXTL package of programs. The structure was solved using 3055 unique reflections with $I > 2\sigma I$.

The coordinates of the nickel ion and two sulfur atoms were determined from a sharpened Patterson map. The remaining atoms were located by repeated cycles of difference Fourier synthesis and least-squares refinement. All of the hydrogen atoms, except for those on the coordinated water molecule, were included as fixed atoms with isotropic thermal parameters set to 6/5 that of the bound carbon by repeated cycles of difference Fourier synthesis and least-squares refinement. The hydrogen atoms on the coordinated water molecule were refined isotropically with fixed H–O bonds of 0.90 Å to give a final H–O–H angle of 102.5°.

Block-cascade least-square refinement with anisotropic thermal parameters for all non-hydrogen atoms gave final agreement factors of R = 5.79 and R_w = 6.15% for 406 variables*. The free *o*-nitro group on the bound picrate is slightly disordered, as indicated by large anisotropic thermal parameters. The nitromethane of solvation is disordered over a center of symmetry and was fit as a NO_2 group with the N atom at full occupancy and the oxygen atoms at ½ occupancy.

The highest peak in the final difference Fourier map had an electron density of 0.90 $e^-/Å^3$ and was located near the disordered nitro group. The highest peak independent of the disordered nitro group was 0.43 $e^-/Å^3$. Final atomic coordinates and thermal parameters are given in Table II.

Results and Discussion

The essentially octahedral coordination sphere around the nickel ion comprises a facially coordinating trithianonane, a bidentate picrate coordinating through an *o*-nitrophenolate group, and a water molecule (Fig. 1). No unusual bond lengths or angles are found. The Ni–S bond lengths range from 2.392(2) to 2.418(2) Å and agree with those found in [Ni(II)(hexathia-18-crown-6)](picrate)$_2$ [4], dibromo Ni(II)(1,11-diamino-3,6,9-trithiaundecane) [5] and dichloro Ni(II)bis(1,5-dithiacyclooctane) [6]. The Ni–OH_2 bond length (2.030(5) Å) is identical to those in the hexaquo ions in nickel sulfate and nickel ammonium sulfate [7]. Similarly,

TABLE II. Atomic Coordinates ($\times 10^4$) and Temperature Factors (Å $\times 10^3$) for [Ni(trithianonane)(picrate)(H_2O)]-(picrate)

Atom	*x*	*y*	*z*	U^a
Ni	9475(1)	1583(1)	1127(1)	31(1)
S(2)	8112(1)	346(2)	1533(1)	42(1)
S(5)	9511(1)	3335(2)	1805(1)	45(1)
S(8)	8073(1)	3025(2)	0617(1)	40(1)
O(1)	9395(4)	41(5)	580(2)	48(2)
O(11)	10752(3)	532(4)	1532(2)	38(1)
O(121)	10731(3)	2625(5)	807(2)	52(2)
O(122)	12292(4)	3500(8)	693(3)	129(3)
O(141)	15705(4)	2523(7)	1700(3)	97(3)
O(142)	15843(4)	924(7)	2289(2)	85(2)
O(161)	12619(6)	−2032(8)	2429(3)	113(3)
O(162)	11237(5)	−736(9)	2481(3)	131(4)
N(12)	11761(4)	2691(7)	926(2)	56(2)
N(14)	15307(4)	1607(7)	1939(2)	57(2)
N(16)	12070(4)	−960(7)	2321(2)	55(2)
C(1)	8600(6)	−1477(8)	1570(4)	72(3)
C(3)	8570(6)	935(8)	2178(3)	57(3)
C(4)	8576(6)	2502(8)	2220(3)	58(3)
C(6)	8604(5)	4712(7)	1497(3)	49(2)
C(7)	7656(5)	4163(8)	1112(3)	50(2)
C(9)	8781(6)	4295(8)	265(3)	57(3)
C(11)	11776(4)	828(6)	1608(2)	28(2)
C(12)	12347(4)	1864(6)	1339(2)	33(2)
C(13)	13489(5)	2110(7)	1443(2)	38(2)
C(14)	14111(4)	1330(7)	1823(2)	36(2)
C(15)	13649(5)	308(7)	2100(2)	39(2)
C(16)	12518(5)	92(6)	1999(2)	34(2)
O(21)	3532(4)	4194(6)	4587(2)	59(2)
O(221)	1998(6)	5459(10)	5126(3)	157(4)
O(222)	584(6)	6032(8)	4637(3)	129(4)
O(241)	−1211(5)	2205(8)	3626(3)	110(3)
O(242)	−269(6)	607(9)	3325(3)	112(3)
O(261)	3638(6)	918(11)	3554(3)	162(5)
O(262)	4571(5)	2124(7)	4140(3)	83(3)
N(22)	1439(5)	5220(7)	4769(3)	69(3)
N(24)	−339(6)	1664(9)	3577(3)	65(3)
N(26)	3693(5)	1804(7)	3885(3)	63(3)
C(21)	2666(5)	3597(7)	4355(2)	38(2)
C(22)	1557(5)	4061(7)	4422(3)	46(2)
C(23)	604(5)	3480(8)	4165(3)	50(2)
C(24)	679(5)	2353(8)	3833(3)	47(2)
C(25)	1690(6)	1825(7)	3751(2)	49(2)
C(26)	2655(5)	2417(7)	4000(2)	43(2)
Ha	9929(39)	−548(57)	498(25)	57
Hb	8995(46)	232(73)	271(11)	57
Ns	5237(9)	5578(12)	−127(4)	150(4)
Osa	5834(10)	6258(14)	218(5)	92(4)
Osb	4913(13)	4451(18)	560(6)	121(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor for all atoms except Ha, Hb, Ns, Osa, and Osb, which were refined isotropically.

---

*$R = \Sigma(||F_o| \quad |F_c||)/\Sigma|F_o|$; $R_w = \Sigma(w^{1/2}|F_o| - |F_c|)/\Sigma w^{1/2}F_o$; G.O.F. (Goodness of Fit) = $[\Sigma w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$.

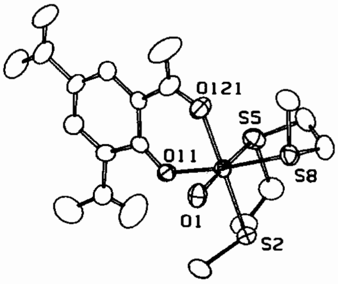
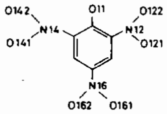


Fig. 1. ORTEP drawing of the [Ni(trithianonane)(picrate)-$(H_2O)]^{2+}$ cation showing thermal ellipsoids at 50% probability level (hydrogen atoms are omitted for clarity). Numbering of atoms in the trithianonane group follows IUPAC convention, *i.e.*, atoms are numbered sequentially (C1, S2, C3, etc.) Atoms on the bound picrate group are numbered as follows:



(those on the free picrate are numbered analogously with the phenolic oxygen atom being O(21), etc.).

the nickel–phenolate bond length (2.003(4) Å) compares closely with those found in previous structures [8, 9]. Although to our knowledge no structures with a Ni(II)–(organic nitro group) bond have been published for comparison, the observed Ni–O(121) bond length of 2.088(5) Å is only slightly longer than other Ni–O bond lengths. Finally, bond lengths and angles in the trithianonane ligand (Table III) are similar to those reported previously in [Co(II)(trithianonane)$_2$]$^{2+}$ cation [2].

Coordination to the Ni(II) ion does not greatly change the geometry of the coordinated picrate ion from that in free picrates. For example, the C–O-(phenolic) distance of 1.258(6) Å compares closely with that of 1.264(7) Å for the free picrate in the same unit cell. Carbon–carbon bond lengths also agree closely. The similarity of these values is less surprising than would appear on first sight since the phenolic oxygen atom in the free picrate hydrogen-bonds to protons on the bound water molecule, and, hence, in a sense it too is bound.

In both the free and bound picrates one of the NO_2 groups rotates significantly (by 33.6 and 39.4°, respectively) out of the plane of the carbon atoms.

TABLE III. Bond Lengths (Å) and Angles (°) for [Ni(trithianonane)(picrate)(H_2O)] (picrate)

Ni–S(2)	2.392(2)	Ni–S(5)	2.418(2)
Ni–O(1)	2.030(5)	Ni–O(11)	2.003(4)
Ni–O(121)	2.088(5)	Ni–S(8)	2.416(2)
S(2)–C(1)	1.805(7)	S(2)–C(3)	1.792(7)
S(5)–C(4)	1.857(8)	S(5)–C(6)	1.807(7)
S(8)–C(9)	1.801(8)	S(8)–C(7)	1.811(7)
O(1)–Hb	0.900(37)	O(1)–Ha	0.900(55)
O(11)–C(11)	1.258(6)	N(12)–C(12)	1.434(8)
O(121)–N(12)	1.243(6)	O(122)–N(12)	1.215(10)
O(141)–N(14)	1.205(9)	O(142)–N(14)	1.225(8)
O(161)–N(16)	1.215(9)	O(162)–N(16)	1.168(9)
N(14)–C(14)	1.459(7)	N(16)–C(16)	1.455(9)
C(3)–C(4)	1.472(11)	C(6)–C(7)	1.505(9)
C(11)–C(12)	1.437(8)	C(11)–C(16)	1.437(7)
C(12)–C(13)	1.390(8)	C(15)–C(16)	1.372(8)
C(13)–C(14)	1.370(8)	C(14)–C(15)	1.371(9)
O(21)–C(21)	1.264(7)	O(221)–N(22)	1.097(10)
O(222)–N(22)	1.291(10)	O(241)–N(24)	1.195(10)
O(242)–N(24)	1.202(11)	O(261)–N(26)	1.197(12)
O(262)–N(26)	1.209(8)	N(22)–C(22)	1.437(10)
N(24)–C(24)	1.465(9)	N(26)–C(26)	1.454(9)
C(21)–C(22)	1.449(9)	C(21)–C(26)	1.446(9)
C(22)–C(23)	1.363(9)	C(23)–C(24)	1.380(10)
C(24)–C(25)	1.368(10)	C(25)–C(26)	1.370(9)
Ns–Osa	1.248(16)	Ns–Nsa	1.436(24)
Ns–Osba	1.126(19)	Osb–Nsa	1.126(19)
S(2)–Ni–S(5)	86.5(1)	S(2)–Ni–O(1)	90.4(1)
S(5)–Ni–O(1)	176.9(1)	S(2)–Ni–O(11)	93.2(1)
S(5)–Ni–O(11)	90.8(1)	O(1)–Ni–O(11)	88.8(2)

(continued overleaf)

TABLE III. *(continued)*

S(2)–Ni–O(121)	176.8(1)	S(5)–Ni–O(121)	92.5(1)
O(1)–Ni–O(121)	90.5(2)	O(11)–Ni–O(121)	83.8(2)
S(2)–Ni–S(8)	92.5(1)	S(5)–Ni–S(8)	87.9(1)
O(1)–Ni–S(8)	92.8(1)	O(11)–Ni–S(8)	174.1(1)
O(121)–Ni–S(8)	90.5(1)	Ni–S(2)–C(1)	103.9(3)
Ni–S(2)–C(3)	97.8(2)	C(1)–S(2)–C(3)	100.8(4)
Ni–S(5)–C(4)	101.6(2)	Ni–S(5)–C(6)	102.2(2)
C(4)–S(5)–C(6)	100.3(3)	Ni–S(8)–C(7)	100.2(2)
Ni–S(8)–C(9)	107.8(2)	C(7)–S(8)–C(9)	100.7(3)
Ni–O(1)–Ha	130.1(33)	Ni–O(1)–Hb	117.4(42)
Ha–O(1)–Hb	102.5(53)	Ni–O(11)–C(11)	130.0(4)
Ni–O(121)–N(12)	133.4(4)	O(122)–N(12)–C(12)	118.6(5)
O(122)–N(12)–O(12)	119.4(6)	C(12)–N(12)–O(12)	122.0(6)
O(141)–N(14)–O(142)	123.7(6)	O(141)–N(14)–C(14)	118.6(5)
O(142)–N(14)–C(14)	117.7(6)	O(161)–N(16)–O(162)	122.5(8)
O(161)–N(16)–C(16)	117.2(6)	O(162)–N(16)–C(16)	120.2(7)
S(2)–C(3)–C(4)	112.0(5)	S(5)–C(4)–C(3)	111.9(5)
S(5)–C(6)–C(7)	114.2(5)	C(6)–C(7)–S(8)	114.7(5)
O(11)–C(11)–C(12)	127.2(5)	O(11)–C(11)–C(16)	120.4(5)
C(12)–C(110–C(16)	112.4(5)	N(12)–C(12)–C(13)	115.3(5)
N(12)–C(12)–C(11)	121.2(5)	C(13)–C(12)–C(11)	123.5(5)
C(12)–C(11)–C(16)	118.7(6)	N(14)–C(14)–C(13)	118.7(6)
N(14)–C(14)–C(15)	118.9(5)	C(13)–C(14)–C(15)	122.4(5)
C(14)–C(15)–C(16)	118.3(5)	N(16)–C(16)–C(15)	115.8(5)
N(16)–C(16)–C(11)	119.5(5)	C(15)–C(16)–C(11)	124.7(6)
O(221)–N(22)–O(222)	118.7(8)	O(221)–N(22)–C(22)	126.1(7)
O(222)–N(22)–C(22)	115.2(6)	O(241)–N(24)–O(242)	122.9(7)
O(241)–N(24)–C(24)	117.5(7)	O(242)–N(24)–C(24)	119.6(7)
O(261)–N(26)–O(262)	121.7(7)	O(261)–N(26)–C(26)	117.9(6)
O(262)–N(26)–C(26)	120.2(6)	O(21)–C(21)–C(22)	121.9(6)
O(21)–C(21)–C(26)	125.3(6)	C(22)–C(21)–C(26)	112.8(5)
N(22)–C(22)–C(21)	119.0(5)	N(22)–C(22)–C(23)	117.4(6)
C(21)–C(22)–C(23)	123.5(6)	C(22)–C(23)–C(24)	119.3(6)
N(24)–C(24)–C(23)	119.9(6)	N(24)–C(24)–C(25)	118.8(6)
C(23)–C(24)–C(25)	121.3(6)	C(24)–C(25)–C(26)	120.0(6)
N(26)–C(26)–C(21)	120.7(5)	N(26)–C(26)–C(25)	116.4(6)
C(21)–C(26)–C(25)	122.9(6)	Osa–Ns–Nsa	106.0(13)
Osa–Ns–Osba	137.4(15)	Nsa–Ns–Osba	115.8(15)

The remaining nitro groups, including the one bound to Ni(II), remain within 10° of coplanarity with the aromatic ring. Rotated *o*-nitro groups are commonly observed in picrates, and have been attributed to steric hindrance between the phenolic and nitro oxygen atoms [11]. However, the presence of twisted nitro groups in non-phenolic nitroaromatic compounds [12] and their absence in the *o*-nitro groups of a picrate structure [13] cast doubt on this explanation. In the present compound both *o*-nitro groups of the free picrate are oriented such that each hydrogen-bonds in a chelating fashion to one proton on the coordinated water molecule (O–H–––O distances are 2.73 and 3.05 Å).

Finally, the constriction of the O(11)–Ni–O(121) angle from the ideal value of 90° to 83° indicates the bite of the *o*-nitrophenolate group is slightly small for the Ni(II) ion. This observation is consistent with the structures of the *o*-nitrophenolate complexes Co(II) [13] and Mn(I) [1], which have average O–M–O angles of 79.8 and 85.9(4)°, respectively.

Acknowledgements

We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The purchase of the diffractometer was supported in part by NSF grant CHE 8000670.

References

1 R. G. Little, *Acta Crystallogr., Sect. B:, 25,* 2398 (1979).

2 J. R. Hartman, E. J. Hintsa and S. R. Cooper, submitted for publication.

3 D. T. Cromer and J. T. Weber, 'International Tables for X-ray Crystallography, Vol. IV', Kynoch Press, Birmingham, 1974.

4 E. J. Hintsa, J. R. Hartmann and S. R. Cooper, *J. Am. Chem. Soc., 105,* 3738 (1983).

5 M. G. B. Drew, D. A. Rice and K. M. Richards, *J. Chem. Soc., Dalton Trans.,* 2503 (1980).

6 N. A. Hill and H. Hope, *Inorg. Chem., 13,* 2079 (1974).

7 R. W. G. Wyckoff, 'Crystal Structures, Vol. 3, 2nd edn.', Interscience Publishers, New York, 1965.

8 D. P. Freyberg, G. M. Mockler and E. Sinn, *Inorg. Chem., 18,* 808 (1979).

9 J. I. Bullock, M. F. C. Ladd and D. C. Povey, *J. Chem. Soc., Dalton Trans.,* 2242 (1977).

10 E. Carstensen-Oeser, S. Gottlicher and G. Habermehl, *Chem. Ber., 101,* 1648 (1968).

11 K. Maartmann-Moe, *Acta Crystallogr., Sect. B:, 25,* 1452 (1969).

12 C. S. Choi and J. E. Abel, *Acta Crystallogr., Sect. B:, 28,* 193 (1972).

13 V. G. Andrianov, Yu. T. Struchkov, N. I. Pyshnograeva, V. N. Setkina and D. N. Kursanov, *J. Organomet. Chem., 206,* 177 (1981).,