Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Tetraphenylarsonium diisothiocyanatodibromonickelate(II)

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.007 Å
R factor = 0.042
wR factor = 0.141
Data-to-parameter ratio = 16.6

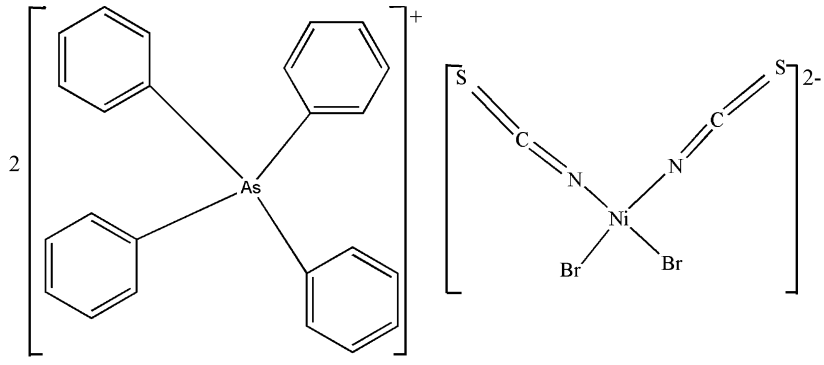
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 22 February 2006
Accepted 20 March 2006

Use of mixed-ligand (bromide and thiocyanate ions) coordination with nickel has led to the crystallization of the title compound, $(C_{24}H_{20}As)_2[Ni(NCS)_2Br_2]$. X-ray crystal structure analysis reveals that the asymmetric unit contains one $(C_6H_5)_4As^+$ cation and one half $[Ni(NCS)_2Br_2]^{2-}$ anion, the latter lying on a crystallographic twofold axis.

Comment

In view of our interest in the rational synthesis of mixed-ligand complex salts, for the first time single-crystal X-ray studies were conducted on mixed diisothiocyanatodibromonickelate(II) salts. The title compound, (I), and its analogues have been reported in the literature (Prasad *et al.*, 1982). Studies of the reported compounds were limited to IR and UV spectroscopic techniques. Although the structures of simple tetrachloro-, tetraisothiocyanato-nickelates (II), and mixed tetrahalonickelates(II) are well known, a Cambridge Structural Database (Version 5.26, ConQuest Version 1.7; Allen, 2002) search showed that only a few tetrabromonickelate-based crystal structures are known so far (Bellefeuille *et al.*, 1998; Yamochi *et al.*, 2002). A comparison of the Br—Ni—Br bond angle in dibromodiisothiocyanatonickelate with that in tetrabromonickelate (Hitchcock *et al.*, 2003) shows that the replacement of two bromides with isocyanates increases this angle from 103.92 (5) to 122.37 (4)°. This is expected in view of the larger size of the bromide ligand compared to that of the nitrogen of the thiocyanate ligand. A crystallographic twofold rotation axis passes through the Ni atom.



(I)

Experimental

One of the starting materials, nickel(II) thiocyanate, was prepared in absolute ethanol by the metathetical reaction of $Ni(NO_3)_2{\cdot}6H_2O$ (0.290 g) and KNCS (0.194 g) in the presence of a small amount of triethyl orthoformate. The title compound was prepared from the

interaction of nickel(II) thiocyanate (0.174 g) and $(C_6H_5)_4AsBr$ (0.463 g) in a 1:2 molar ratio in a 2:1 (*v*/*v*) mixture of acetonitrile and absolute ethanol. The compound obtained was recrystallized from acetonitrile. The crystals were isolated, washed with a small amount of acetonitrile and then with diethyl ether and dried in an open-air oven at 363–373 K.

Crystal data

$(C_{24}H_{20}As)_2[NiBr_2(CNS)_2]$	D_x = 1.540 Mg m^{-3}
M_r = 1101.31	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 7590 reflections
a = 13.5382 (10) Å	θ = 2.4–27.2°
b = 15.7796 (11) Å	μ = 3.60 mm^{-1}
c = 23.0555 (16) Å	T = 273 (2) K
β = 105.347 (1)°	Plate, green
V = 4749.7 (6) Å^3	0.35 × 0.22 × 0.10 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	4430 independent reflections
	3556 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.077
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	θ_{max} = 25.5°
	$h = -16 \rightarrow 16$
T_{min} = 0.401, T_{max} = 0.711	$k = -18 \rightarrow 19$
17670 measured reflections	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0881P)^2 + 1.9894P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.042	
$wR(F^2)$ = 0.141	
S = 1.08	$(\Delta/\sigma)_{max}$ = 0.002
4430 reflections	$\Delta\rho_{max}$ = 0.99 e Å^{-3}
267 parameters	$\Delta\rho_{min}$ = −0.88 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

As1—C1	1.902 (4)	As1—C7	1.912 (4)
As1—C19	1.911 (4)	Ni1—N1	1.973 (5)
As1—C13	1.911 (4)	Ni1—Br1	2.3787 (6)
C1—As1—C19	110.05 (17)	C13—As1—C7	106.97 (16)
C1—As1—C13	111.13 (17)	N1—Ni1—N1^{i}	105.2 (3)
C19—As1—C13	109.14 (18)	N1—Ni1—Br1^{i}	110.11 (13)
C1—As1—C7	107.25 (16)	N1—Ni1—Br1	103.98 (13)
C19—As1—C7	112.29 (17)	Br1^{i}—Ni1—Br1	122.37 (4)

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

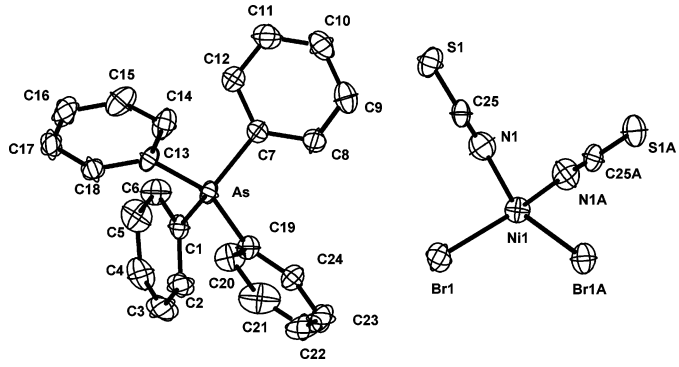


Figure 1
A view of the title compound, showing 50% probability displacement ellipsoids. Atoms labelled with the suffix A were generated by the symmetry code $(2-x, y, \frac{1}{2}-z)$. H atoms have been omitted.

H atoms were treated as riding atoms, with C—H distances of 0.93 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000) and *DIAMOND* (Klaus, 1999); software used to prepare material for publication: *SHELXTL*.

AR acknowledges DST, Government of India, for funding a single-crystal diffractometer under FIST to the Department of Chemistry, IIT, Delhi.

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