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References

CAPELLE, B., DARTIGUENAVE, M., DARTIGUENAVE, Y. & BEAUCHAMP, A. L. (1983). *J. Am. Chem. Soc.* **105**, 4662–4670.

CHIU, K. W., WILKINSON, G., THORNTON-PETT, M. & HURSTHOUSE, M. B. (1984). *Polyhedron*, **3**, 79–85.
 FRENZ, B. A. AND ASSOCIATES (1981). *Structure Determination Package*, 4th edition. College Station, Texas 77840, USA, and Enraf-Nonius, Delft, Holland.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 IBERS, J. A. (1968). *J. Organomet. Chem.* **14**, 423–428.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 JONES, R. A., NORMAN, N. C., SEEGER, M. H., ATWOOD, J. L. & HUNTER, W. E. (1983). *Organometallics*, **2**, 1629–1634.
 KLEIN, H. F. & KARSCH, H. H. (1975). *Inorg. Chem.* **14**, 473–477.
 SLAUGH, L. H. & MULLINEAUX, R. D. (1968). *J. Organomet. Chem.* **13**, 469–477.

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Structure of the 1:2 Complex of Cobalt(II) with 2,3-Naphthosemiquinone Diimine Anion

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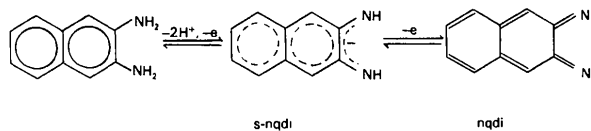
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Abstract. [Co(C₁₀H₈N₂)₂], $M_r = 371.31$, triclinic, $P\bar{1}$, $a = 5.813$ (3), $b = 7.8818$ (9), $c = 16.985$ (2) Å, $\alpha = 84.61$ (1), $\beta = 83.83$ (2), $\gamma = 85.65$ (3)°, $V = 768.58$ Å³, $Z = 2$, $D_m = 1.60$, $D_x = 1.60$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu = 1.122$ mm⁻¹, $F(000) = 382$, $T = 298$ K, final $R = 0.041$ for 2036 observed reflections. The unit cell contains two independent molecules, each lying on a crystallographic inversion center. The complex molecules are nearly planar and packed in a parallel fashion along the a axis. The structure reveals the delocalized bond pattern of the 2,3-naphthosemiquinone diimine anion ligand.

Introduction. It is particularly interesting that the transition-metal complexes with highly delocalized unsaturated electron-rich ligands have unusual properties; they are intensely colored, have an extensive electrochemistry (Balch & Holm, 1966), and possibly contain metal–metal bonds (Peng & Goedken, 1976; Peng, Liaw, Wang & Simon, 1985). The extent of π -electron delocalization over the unsaturated electron-rich ligand moiety is also a novel structural property. Examples of this type are metal complexes of dithiene (Teo & Snyder-Robinson, 1979), *o*-benzoquinone diimine anion (bqdi) (Hall & Soderberg, 1968; Christoph & Goedken, 1973; Peng, Chen, Liaw, Chen

& Wang, 1985), diiminosuccinonitrilo anion (Peng, Wang & Chiang, 1984; Peng, Liaw, Wang & Simon, 1985), and macrocyclic anions (Peng & Goedken, 1976; Peng, Ibers, Miller & Holm, 1976).

2,3-Naphthalenediamine can be oxidized under basic conditions to form 2,3-naphthosemiquinone diimine anion (s-nqdi) and 2,3-naphthoquinone diimine (nqdi).



The title complex was synthesized by air oxidation of 2,3-naphthalenediamine and cobalt(II) acetate in *N,N*-dimethylformamide (DMF) solution. The structure was determined in order to elucidate the structural properties of the s-nqdi ligand.

Experimental. Crystals of [Co(s-nqdi)₂] obtained by slow formation of the complex in DMF solution. Crystal 0.02 × 0.1 × 0.7 mm. CAD-4 diffractometer. D_m measured by flotation. Absorption correction according to the experimental ψ rotation. $2\theta_{\text{max}} = 60^\circ$ ($0 \leq h \leq 8$, $-11 \leq k \leq 11$, $-23 \leq l \leq 23$). Unit cell: least-squares refinement of 25 reflections ($15 < 2\theta < 25^\circ$). Three standard reflections, <2% variation. 4864

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total reflections measured, 2036 with $I \geq 2\sigma(I)$. $R = 0.041$, $wR = 0.044$, $S = 1.38$ based on F_o , 293 variables. $w = 1/[\sigma^2(F_o) + (0.01F_o)^2]$. Structure obtained by Fourier synthesis with Co atoms at $\bar{1}$. H atoms found on difference Fourier synthesis refined by least-squares process. $(\Delta/\sigma)_{\max} = 0.08$. Peaks on final $\Delta\rho$ map $\leq |0.3| e \text{ \AA}^{-3}$. Atomic scattering factors calculated by the analytical form using the coefficients in *International Tables for X-ray Crystallography* (1974). Programs from NRCC PDP-11 package (Gabe & Lee, 1981).

Discussion. Atomic positional parameters and equivalent isotropic temperature factors are listed in Table 1.* Fig. 1 shows the two independent molecules with the labeling scheme and selected bond distances and angles. A diagram of the contents of the unit cell is shown in Fig. 2. All chemically equivalent bond distances and angles in the two molecules are essentially identical. The complex is planar with a maximum deviation of 0.147 (5) Å [C(5A)] for molecule A, and 0.029 (4) Å [N(1B)] for molecule B from the plane formed by all the non-H atoms of each molecule. The complex can be described as having D_{2h} symmetry within experimental error.

* Lists of anisotropic temperature factors, structure factors, H-atom parameters, and bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42643 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters x , y , z and B_{eq}

	x	y	z	B_{eq} *(Å ²)
CoA	0	0	0	2.58 (3)
CoB	$\frac{1}{2}$	$\frac{1}{2}$	0	2.59 (3)
N(1A)	0.0901 (6)	-0.1527 (4)	0.0785 (2)	2.86 (14)
N(2A)	-0.2741 (6)	0.0164 (4)	0.0632 (2)	2.71 (13)
N(1B)	0.5696 (6)	0.4954 (4)	0.1017 (2)	2.83 (14)
N(2B)	0.2528 (6)	0.3835 (4)	0.0442 (2)	2.85 (14)
C(1A)	-0.0631 (7)	-0.1762 (5)	0.1442 (2)	2.43 (14)
C(2A)	-0.0351 (7)	-0.2741 (5)	0.2147 (2)	2.72 (16)
C(3A)	-0.2104 (7)	-0.2757 (5)	0.2771 (2)	2.45 (15)
C(4A)	-0.1815 (7)	-0.3684 (5)	0.3518 (3)	3.10 (18)
C(5A)	-0.3516 (8)	-0.3679 (6)	0.4131 (3)	3.63 (20)
C(6A)	-0.5645 (9)	-0.2734 (6)	0.4030 (3)	3.93 (20)
C(7A)	-0.6007 (8)	-0.1829 (5)	0.3333 (3)	3.34 (18)
C(8A)	-0.4278 (6)	-0.1811 (5)	0.2678 (2)	2.44 (15)
C(9A)	-0.4573 (7)	-0.0838 (5)	0.1957 (2)	2.75 (16)
C(10A)	-0.2805 (7)	-0.0770 (5)	0.1346 (2)	2.54 (15)
C(1B)	0.4245 (7)	0.4128 (4)	0.1586 (2)	2.37 (15)
C(2B)	0.4394 (7)	0.3884 (5)	0.2398 (2)	2.66 (16)
C(3B)	0.2705 (7)	0.3031 (5)	0.2889 (2)	2.53 (15)
C(4B)	0.2762 (8)	0.2755 (5)	0.3726 (3)	3.16 (17)
C(5B)	0.1090 (9)	0.1956 (6)	0.4202 (3)	3.67 (20)
C(6B)	-0.0808 (8)	0.1361 (6)	0.3875 (3)	3.48 (18)
C(7B)	-0.0926 (7)	0.1584 (5)	0.3076 (3)	3.04 (18)
C(8B)	0.0781 (7)	0.2417 (5)	0.2556 (3)	2.75 (16)
C(9B)	0.0650 (7)	0.2667 (5)	0.1733 (3)	2.65 (16)
C(10B)	0.2337 (7)	0.3500 (5)	0.1246 (2)	2.46 (15)

* B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

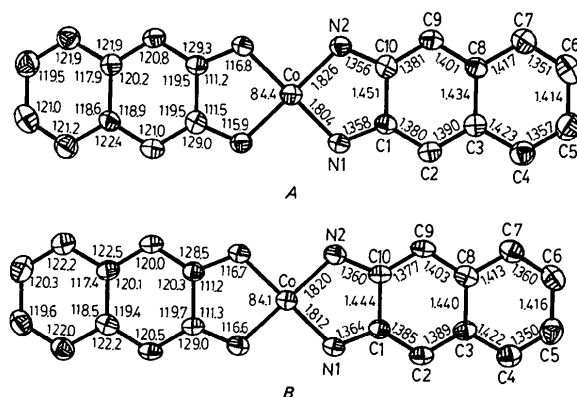


Fig. 1. ORTEP plot (Johnson, 1965) of the $[\text{Co}(\text{s-nqdi})_2]$ molecule with a labeling diagram and selected interatomic distances (Å) and angles ($^\circ$). The thermal ellipsoids are drawn to the 50% probability level. The e.s.d.'s are as follows: Co-N distances, 0.003 Å; C-N and C-C distances, 0.005–0.006 Å; N-Co-N angles, 0.1 $^\circ$; Co-N-C, N-C-C and C-C-C angles, 0.2–0.3 $^\circ$.

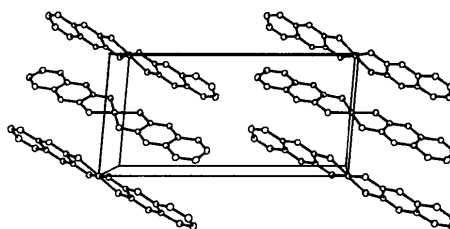
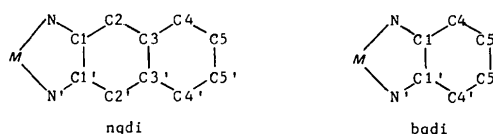


Fig. 2. Packing diagram of the molecules in the unit cell.

Table 2. Comparison of corresponding bond distances (Å) and angles ($^\circ$) in $[\text{Co}(\text{s-nqdi})_2]$, $[\text{Co}(\text{s-bqdi})_2]$, $[\text{Ni}(\text{s-bqdi})_2]$ and $[\text{Fe}(\text{bqdi})_3]^{2+}$



All the bond distances and angles listed are the average of all chemically equivalent ones.

	$[\text{Co}(\text{s-nqdi})_2]$	$[\text{Co}(\text{s-bqdi})_2]$	$[\text{Ni}(\text{s-bqdi})_2]$	$[\text{Fe}(\text{bqdi})_3]^{2+}$
M-N	1.816 (3)	1.824 (5)	1.83 (1)	1.916 (5)
N-C(1)	1.360 (5)	1.358 (8)	1.38 (2)	1.300 (8)
C(1)-C(1')	1.448 (5)	1.423 (9)	1.41 (2)	1.455 (9)
C(1)-C(2)	1.381 (5)			
C(2)-C(3)	1.396 (5)			
C(3)-C(3')	1.437 (5)			
C(3)-C(4)	1.419 (5)	1.412 (9)	1.41 (2)	1.434 (9)
[C(1)-C(4)]				
C(4)-C(5)	1.355 (6)	1.361 (10)	1.37 (2)	1.339 (9)
C(5)-C(5')	1.415 (7)	1.403 (11)	1.43 (2)	1.423 (10)
N-M-N'	84.2 (1)	84.2 (2)	85.9 (7)	79.4 (2)
M-N-C(1)	116.5 (2)	116.0 (4)	114 (1)	117.8 (4)
N-C(1)-C(1')	113.3 (3)	111.9 (5)	113 (1)	112.4 (5)
Reference	This Work	Peng, Chen, Liaw, Chen & Wang (1985)	Hall & Soderberg (1968)	Peng, Chen, Liaw, Chen & Wang (1985)

The complex exhibits the delocalized bond pattern of the s-nqdi ligand, which is similar to that of [Co(s-bqdi)₂] (Peng, Chen, Liaw, Chen & Wang, 1985) and of [Ni(s-bqdi)₂] (Hall & Soderberg, 1968) (Table 2). The average Co—N distance, 1.816 (3) Å, which is comparable to those in [Co(s-bqdi)₂] and [Ni(s-bqdi)₂], is short indicating a strong interaction between the Co atom and s-nqdi ligands. The average N—C(1) distance, 1.360 (5) Å, is very close to the aromatic C—N distance of pyridine. As for the C—C distances, the C(4)—C(5) distance, 1.355 (6) Å, is the shortest, but still comparable to those in corresponding naphthalene, 1.36 Å, and s-bqdi ligands (Table 2). The degree of delocalization is greater than that observed in [Fe(bqdi)₃]²⁺ (Peng, Chen, Liaw, Chen & Wang, 1985).

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Structure of Sodium Iodide–Acetonitrile–Water (2/3/3)

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Abstract. NaI.1½H₂O.1½C₂H₃N, *M*_r = 238.50, hexagonal, *P*62*m*, *a* = 8.707 (1), *c* = 6.424 (1) Å, *V* = 421.8 (1) Å³, *Z* = 2, *D*_x = 1.878 g cm⁻³, *Mo Kα*, λ = 0.71069 Å, μ = 38.21 cm⁻¹, *F*(000) = 224, *T* = 293 (1) K, final *R* = 0.032 for 288 non-zero reflections. Each sodium cation is octahedrally coordinated to three waters and three acetonitriles. Sodium-centred octahedra share opposite faces with two adjacent octahedra to form continuous chains. The shared faces consist of either three nitrogens or three oxygens, alternately along the chain, and in phase from one chain to another. Each iodide is at the centre of a trigonal prism on whose triangular-face edges are located acetonitrile molecules with the methyl groups nearest to the anions. In the equatorial plane of each prism lie the oxygens of three water molecules, which are bound to the iodides by I···H—O interactions, creating an effective coordination number of nine for iodide. Adjacent prisms, which share a common square face, are respectively left- and right-handed owing to the

different orientations of the acetonitriles. The sodium–iodide internuclear separations (5.270 Å) are even greater than the iodide–iodide contacts (5.027 Å) and are clearly nonbonding.

Introduction. In the course of Raman spectroscopic studies of alkali halides in aqueous and non-aqueous media (Irish, Hill, Archambault & Atkinson, 1985) we discovered, in the mixed-solvent system H₂O—CH₃CN and in the presence of sodium iodide, that crystals grew inside the sealed Raman capillary tubes. As sodium iodide is soluble in either water or acetonitrile alone we were intrigued by this result. With some difficulty, as the crystals are rapidly decomposed upon removal of their mother liquor, we have obtained the crystal and molecular structure of NaI.1½H₂O.1½CH₃CN. To our knowledge there are only three previous reports of X-ray-determined structures of compounds containing an alkali halide, water and an organic solvent [LiCl.1,4-dioxane.H₂O (Durant & Griffe, 1968); LiCl.2pyridine.H₂O (Durant, Piret & Van Meerssche, 1967); NaI.2glycine.H₂O (Verbist, Putzeys, Piret & Van

References

- BALCH, A. L. & HOLM, R. H. (1966). *J. Am. Chem. Soc.* **88**, 5201–5209.
CHRISTOPH, G. G. & GOEDKEN, V. L. (1973). *J. Am. Chem. Soc.* **95**, 3869–3875.
GABE, E. J. & LEE, F. L. (1981). *Acta Cryst.* **A37**, S399.
HALL, G. S. & SODERBERG, R. H. (1968). *Inorg. Chem.* **7**, 2300–2303.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
PENG, S. M., CHEN, C. T., LIAW, D. S., CHEN, C. I. & WANG, Y. (1985). *Inorg. Chim. Acta*, **101**, L31–L33.
PENG, S. M. & GOEDKEN, V. L. (1976). *J. Am. Chem. Soc.* **98**, 8500–8510.
PENG, S. M., IBERS, J. A., MILLER, M. & HOLM, R. H. (1976). *J. Am. Chem. Soc.* **98**, 8037–8041.
PENG, S. M., LIAW, D. S., WANG, Y. & SIMON, A. (1985). *Angew. Chem. Int. Ed. Engl.* **24**, 210–211.
PENG, S. M., WANG, Y. & CHIANG, C. K. (1984). *Acta Cryst.* **C40**, 1541–1542.
TEO, B. K. & SNYDER-ROBINSON, R. A. (1979). *Inorg. Chem.* **18**, 1490–1495.

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