Crystal structure of bis(1,10-phenanthroline)diazidocobalt(II), $C_{24}H_{16}CoN_{10}$

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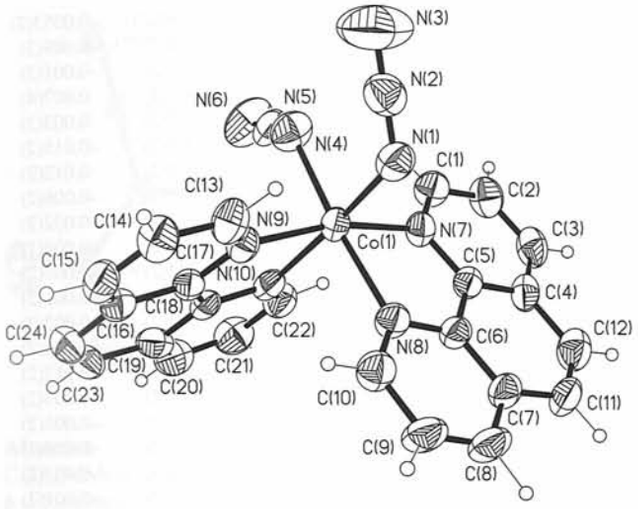

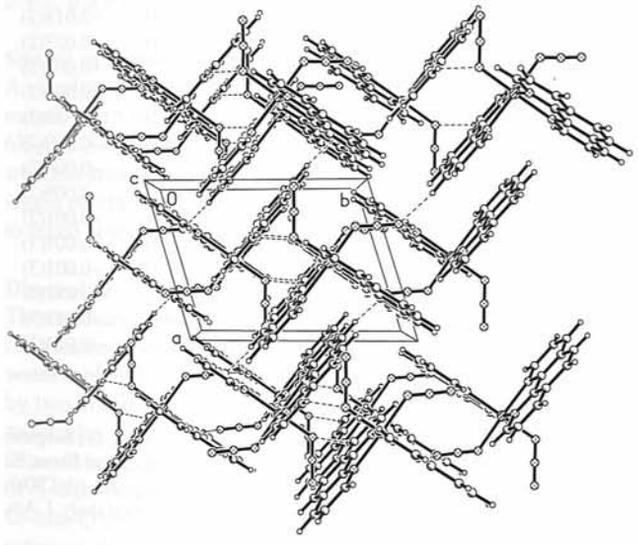

Abstract

$C_{24}H_{16}CoN_{10}$, triclinic, $P\bar{1}$ (No. 2), $a = 8.205(3)$ Å, $b = 11.016(4)$ Å, $c = 12.423(5)$ Å, $\alpha = 82.252(6)°$, $\beta = 82.298(6)°$, $\gamma = 72.481(6)°$, $V = 1055.8$ Å^3, $Z = 2$, $R_{gt}(F) = 0.056$, $wR_{ref}(F^2) = 0.087$, $T = 293$ K.

Source of material

Cobalt(II) sulfate (1.0 mmol) and sodium azide (2.0 mmol) were dissolved in 10 mL water, then a solution of 1,10-phenanthroline(2.0 mmol) in ethanol (10 mL) was slowly added with stirring for four hours at room temperature, and then it was filtered. The filtrate was left to stand for over 10 days until red needle crystals was obtained in 80% yield.

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Discussion

The azide anion is a good bridging ligand for divalent ions, such as Cu(II), Ni(II), Mn(II), etc. In recent years, studies on synthesis and properties of complexes bridged by the pseudohalide azide anion have attracted much attention [1-3], owing to their intriguing structural diversity, potential functions as models for metalloenzymes and ferromagnetic or antiferromagnetic interactions [4-6]. On the other hand, nickel diazide · 2(1,10-phenanthroline) is a monomeric compound [7]. Here we report on another monomeric compound, namely $Co(N_3)_2(Phen)_2$, where Phen is 1,10-phenanthroline.

The molecular unit of the title compound comprises a Co(II) ion, two azide anions and two 1,10-phenanthroline molecules. As shown in top figure, each Co(II) ion is surrounded by two N atoms of two terminal anions and by four N atoms of two 1,10-phenanthroline ligands, [Co—N distances are 2.056(4) Å, 2.077(3) Å, 2.082(3) Å, 2.099(3) Å, 2.110(3) Å, 2.113(3) Å, respectively], forming an distorted CoN_6 octahedron. Azide anions can bind to metal ions in a number of modes, such as a terminal ligand via one nitrogen donor, as a bridge in the end-to-end ($\mu_{1,1}$) manner via one nitrogen donor, and in a end-on ($\mu_{1,3}$) manner via both of the peripheral donor N atoms [8], but in the title compound, azide anions only coordinate Co(II) ion by one mode. It should be noted that the hydrogen-bonding interactions and π-π interactions play an important role in the crystal structure of the title compound, as shown bottom figure. In the 1,10-phenanthroline complex, adjacent molecules are linked by a weak C–H···N interaction [d(C···N) = 3.412(3) Å] to form chains. Moreover, there are strong interchain π-π interactions between the aromatic rings of adjacent chains with the face-to-face separation of ca. 3.43 Å, resulting in an extended three-dimensional supramolecular array.

Table 1. Data collection and handling.

Crystal:	red needle, size 0.09 × 0.28 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.51 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, 580 frames, $\Delta\omega = 2°$
$2\theta_{max}$:	54.54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6300, 4512
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2200
$N(param)_{refined}$:	380
Programs:	SHELX-97 [9], ORTEP-II [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.622(4)	0.184(3)	0.969(2)	0.05(1)
H(2)	2*i*	0.568(4)	0.243(3)	1.152(2)	0.05(1)
H(3)	2*i*	0.349(4)	0.436(3)	1.181(2)	0.04(1)
H(4)	2*i*	–0.105(5)	0.760(4)	0.764(3)	0.08(1)
H(5)	2*i*	–0.004(4)	0.665(3)	0.585(2)	0.05(1)
H(6)	2*i*	0.207(4)	0.476(3)	0.579(2)	0.05(1)
H(7)	2*i*	0.112(5)	0.624(3)	1.114(3)	0.08(1)
H(8)	2*i*	–0.035(5)	0.738(4)	0.961(3)	0.08(2)
H(9)	2*i*	0.598(4)	0.367(3)	0.489(2)	0.05(1)
H(10)	2*i*	0.565(4)	0.306(3)	0.313(3)	0.06(1)
H(11)	2*i*	0.402(6)	0.164(4)	0.304(3)	0.12(2)
H(12)	2*i*	0.069(6)	–0.065(4)	0.773(3)	0.09(2)
H(13)	2*i*	0.129(5)	–0.005(4)	0.941(3)	0.08(1)
H(14)	2*i*	0.299(4)	0.137(3)	0.929(2)	0.04(1)
H(15)	2*i*	0.230(5)	0.025(3)	0.402(3)	0.07(1)
H(16)	2*i*	0.106(4)	–0.065(3)	0.576(2)	0.05(1)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	2*i*	0.48328(7)	0.28827(5)	0.73495(4)	0.0414(3)	0.0302(3)	0.0322(3)	–0.0071(2)	–0.0050(2)	–0.0053(2)
N(1)	2*i*	0.6343(5)	0.4083(3)	0.6853(3)	0.048(3)	0.042(2)	0.065(2)	–0.008(2)	–0.004(2)	–0.009(2)
N(2)	2*i*	0.7838(6)	0.3745(3)	0.6599(3)	0.059(3)	0.053(3)	0.067(3)	–0.019(3)	–0.015(2)	–0.001(2)
N(3)	2*i*	0.9320(7)	0.3440(5)	0.6320(5)	0.061(4)	0.112(4)	0.228(6)	–0.026(3)	–0.002(4)	0.007(4)
N(4)	2*i*	0.6983(4)	0.1311(3)	0.7547(3)	0.058(3)	0.043(2)	0.065(2)	–0.009(2)	–0.003(2)	0.003(2)
N(5)	2*i*	0.7036(4)	0.0346(3)	0.8087(3)	0.050(2)	0.043(2)	0.049(2)	0.003(2)	–0.001(2)	–0.015(2)
N(6)	2*i*	0.7140(5)	–0.0636(3)	0.8620(3)	0.097(4)	0.049(3)	0.080(3)	–0.002(2)	0.004(2)	0.012(2)
N(7)	2*i*	0.4480(4)	0.3282(3)	0.8984(2)	0.047(2)	0.035(2)	0.036(2)	–0.010(2)	–0.007(2)	–0.006(2)
N(8)	2*i*	0.2677(4)	0.4518(3)	0.7324(2)	0.044(2)	0.038(2)	0.038(2)	–0.004(2)	–0.011(2)	–0.002(2)
N(9)	2*i*	0.4612(4)	0.2559(3)	0.5774(2)	0.043(2)	0.033(2)	0.036(2)	–0.007(2)	–0.003(2)	–0.004(1)
N(10)	2*i*	0.3279(4)	0.1632(3)	0.7657(2)	0.035(2)	0.038(2)	0.035(2)	–0.002(2)	0.002(2)	–0.007(2)
C(1)	2*i*	0.5338(6)	0.2646(4)	0.9809(3)	0.052(3)	0.043(3)	0.042(3)	–0.006(2)	–0.014(2)	0.001(2)
C(2)	2*i*	0.4998(6)	0.3031(4)	1.0861(3)	0.070(4)	0.055(3)	0.037(3)	–0.021(3)	–0.013(2)	–0.002(2)
C(3)	2*i*	0.3717(6)	0.4109(4)	1.1072(3)	0.066(3)	0.061(3)	0.035(2)	–0.029(3)	0.002(2)	–0.016(2)
C(4)	2*i*	0.2766(5)	0.4816(4)	1.0216(3)	0.051(3)	0.039(2)	0.043(2)	–0.020(2)	0.005(2)	–0.012(2)
C(5)	2*i*	0.3188(5)	0.4367(3)	0.9186(3)	0.037(2)	0.035(2)	0.038(2)	–0.013(2)	0.003(2)	–0.007(2)
C(6)	2*i*	0.2225(5)	0.5043(3)	0.8294(3)	0.036(2)	0.032(2)	0.046(2)	–0.008(2)	–0.003(2)	–0.005(2)
C(7)	2*i*	0.0904(5)	0.6164(3)	0.8449(3)	0.042(3)	0.031(2)	0.061(3)	–0.010(2)	–0.001(2)	–0.006(2)
C(8)	2*i*	–0.0022(6)	0.6772(4)	0.7554(4)	0.043(3)	0.038(3)	0.080(3)	0.004(2)	–0.010(3)	–0.003(2)
C(9)	2*i*	0.0426(5)	0.6250(4)	0.6584(4)	0.044(3)	0.049(3)	0.066(3)	0.006(2)	–0.014(2)	–0.001(3)
C(10)	2*i*	0.1770(6)	0.5120(4)	0.6496(3)	0.054(3)	0.045(3)	0.048(3)	–0.009(2)	–0.010(2)	–0.003(2)
C(11)	2*i*	0.1404(6)	0.5983(4)	1.0354(4)	0.065(4)	0.056(3)	0.054(3)	–0.021(3)	0.007(3)	–0.018(3)
C(12)	2*i*	0.0532(6)	0.6611(4)	0.9513(4)	0.050(3)	0.041(3)	0.071(3)	–0.006(2)	0.006(3)	–0.023(2)
C(13)	2*i*	0.5287(6)	0.3043(4)	0.4844(3)	0.063(3)	0.037(3)	0.041(3)	–0.011(2)	–0.001(2)	–0.003(2)
C(14)	2*i*	0.5069(6)	0.2753(4)	0.3817(3)	0.064(3)	0.051(3)	0.034(3)	–0.012(2)	–0.007(2)	0.001(2)
C(15)	2*i*	0.4148(6)	0.1918(4)	0.3754(4)	0.058(3)	0.045(3)	0.044(3)	0.000(2)	–0.011(2)	–0.010(2)
C(16)	2*i*	0.3395(5)	0.1391(4)	0.4723(3)	0.038(3)	0.041(2)	0.050(3)	0.003(2)	–0.013(2)	–0.009(2)
C(17)	2*i*	0.3671(5)	0.1748(3)	0.5719(3)	0.036(2)	0.033(2)	0.037(2)	–0.001(2)	–0.012(2)	–0.004(2)
C(18)	2*i*	0.2959(5)	0.1249(3)	0.6739(3)	0.031(2)	0.029(2)	0.047(2)	–0.002(2)	–0.002(2)	–0.009(2)
C(19)	2*i*	0.1979(5)	0.0393(4)	0.6731(3)	0.036(3)	0.045(3)	0.058(3)	–0.010(2)	–0.010(2)	–0.001(2)
C(20)	2*i*	0.1327(6)	–0.0080(4)	0.7755(4)	0.052(3)	0.048(3)	0.078(4)	–0.017(3)	–0.002(3)	–0.004(3)
C(21)	2*i*	0.1697(6)	0.0272(4)	0.8685(4)	0.056(3)	0.058(3)	0.060(3)	–0.019(3)	0.006(3)	–0.001(3)
C(22)	2*i*	0.2683(6)	0.1127(4)	0.8607(3)	0.048(3)	0.052(3)	0.045(3)	–0.011(2)	0.003(2)	–0.011(2)
C(23)	2*i*	0.2422(6)	0.0501(4)	0.4754(4)	0.051(3)	0.055(3)	0.057(3)	–0.012(2)	–0.019(3)	–0.012(3)
C(24)	2*i*	0.1748(6)	0.0033(4)	0.5699(4)	0.045(3)	0.052(3)	0.077(3)	–0.016(2)	–0.016(3)	–0.014(3)

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