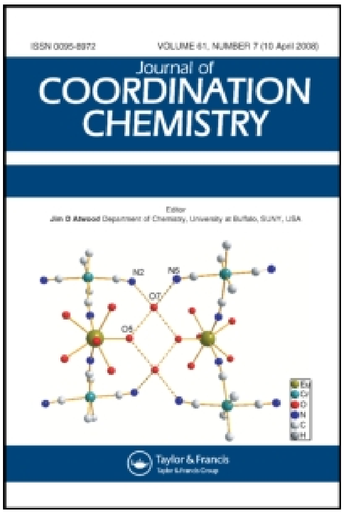

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Syntheses and characterization of mixed-anion cadmium(II) complexes, structural characterization of $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$, as a new eight-coordinate Cd(II) complex

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New mixed-anion cadmium(II) complexes of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) ligands, $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$ and $Cd(bpy)(ClO_4)(CH_3COO)$ have been synthesized and characterized by elemental analysis, IR-, ^{1}H NMR-, ^{13}C- NMR and ^{113}Cd NMR spectroscopy. The single crystal X-ray data of $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$ show the complex to be a monomer and that the Cd atom has an unsymmetrical eight-coordinate geometry, being coordinated by four nitrogen atoms of 'phen' ligands and four oxygen atoms of the nitrite and nitrate anions. There is a short π–π stacking interaction between parallel aromatic rings.

Keywords: Cadmium(II) complexes; Crystal structure; Mixed-anion complexes; π–π stacking

1. Introduction

Cadmium belongs to a category of heavy-metal ions (cadmium, mercury, lead) that have attracted attention over the years, owing to their toxic manifestations in the environment and the various organisms living therein, including plants [1] and humans [2]. Cadmium(II) is found predominantly in minerals and soils in the earth's lithosphere [2, 3]. Non-essential in human physiology, Cd(II) is in competition with Zn(II), from which a number of its toxic effects are believed to arise [4]. In our attempts to synthesize mixed-anion complexes of lead(II) and mercury(II) ions [5–9],

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we became interested in cadmium(II) complexes. In this article, we discuss the synthesis of two mixed-anion cadmium(II) complexes containing 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) ligands, $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$ and $Cd(bpy)(CH_3COO)(ClO_4)$. Mixed-anion complexes that differ in only one part of the coordination sphere are interesting; the importance of the mixed-anion complexes lies in the influence of the replaced ligand on the structure.

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyser. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The ^{113}Cd solution NMR spectra were recorded on a Bruker DRX-500 AVANCE spectrometer at 104.6 MHz using a 5-mm broad-band probe. Cadmium chemical shifts are reported (ppm) downfield from $[Cd(ClO_4)_2 \cdot xH_2O]$ as an external standard.

2.2. *Preparation of $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$*

The complex was prepared by dissolving cadmium(II) acetate (0.230 g, 1 mmol), sodium nitrite (0.138 g, 2 mmol) and sodium nitrate (0.170 g, 2 mmol) in distilled water and adding an alcoholic solution (20 mL) of 1,10-phenanthroline (0.4 g, 2 mmol). The resulting solution was stirred for 3 h at room temperature and then allowed to stand for 2–3 days at *c.* 25°C. Colourless crystals of the product precipitated, which were filtered off, washed with acetone and ether, and air-dried (0.256 g, yield 45%), m.p. 210°C. Found C, 50.30; H, 2.70; N, 14.30. Calcd for $C_{24}H_{16}CdN_6O_{4.35}$; C, 50.48; H, 2.80; N, 14.72%. IR (cm^{-1}) selected bands: $\nu = 721$(s), 842(s), 1091(m), 1232(vs), 1370(m), 1413(s), 1501(m), 1560(m), 1610(s), 3060(w). ^1H NMR (DMSO; δ): 8.00–8.35 (m, 4H), 8.60–9.00 (m, 2H), 9.20–9.40 (m, 2H). ^{13}C-{^1H} NMR (DMSO; δ): 124.58, 127.28, 129.50, 139.23, 144.56, 149.32. ^{113}Cd NMR (DMSO): $\delta = 20.940$ ppm.

2.3. *Preparation of $Cd(bpy)(CH_3COO)(ClO_4)$*

The colourless compound $Cd(bpy)(CH_3COO)(ClO_4)$ was obtained from the reaction of a mixture of $Cd(CH_3COO)_2$ (0.230 g, 1 mmol) and sodium perchlorate (0.123 g, 1 mmol) with 2,2′-bipyridine (0.156 g, 1 mmol). The resulting colourless solution was heated and stirred for about an hour. Then, it was left to evaporate at room temperature, and after a few days, colourless crystals were isolated. (0.267 g, yield 63%), m.p. 230°C. Found C: 33.40; H: 2.40; N: 6.80, whereas the calculated for $C_{12}H_{11}N_2O_6ClCd$ are C: 33.76; H: 2.58; N: 6.56%. IR (cm^{-1}) selected bonds: 624(s), 863(m), 1115(vs), 1420(s), 1596(s), 1645(s), 2983(w), and 3140(w). ^1H NMR (DMSO; δ): 1.60 (s, 3H), 7.80 (t, 2H), 8.20 (q, 2H), 8.70 (d, 2H), and 7.78 (d, 2H). ^{13}C-{^1H} NMR (DMSO; δ): 27.40 ($^{13}CH_3$–COO), 177.80 (CH_3–^{13}COO), 117.55, 124.20, 127.55, 1142.10, 150.20, and 150.60. ^{113}Cd NMR (DMSO): $\delta = 25.750$ ppm.

2.4. *X-ray structure determination*

The intensity data of the title complex were collected using a STOE IPDS 2 diffractometer (Mo–Kα radiation) at 193 K. The structure was solved by direct methods using SIR97 [10] and refined by a full-matrix least-squares procedure (SHELXL–97) [11]. The molecular plots were prepared by using ORTEPIII and WinGX [12], which was also used as an interface during the structure solution procedure. The details of data collection, refinement and crystallographic data are summarized in table 1.

3. Results and discussion

3.1. *Syntheses*

From the reaction between 2,2′-bipyridine (bpy) and mixtures of cadmium(II) acetate with sodium perchlorate, the $Cd(bpy)(CH_3COO)(ClO_4)$ complex was isolated. The IR spectra of this complex show absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1600 cm^{-1} range and $\nu(ClO_4)$ at *c.* 1115 cm^{-1}. The characteristic bands of the acetate anions appear about 1645 ν_{as}(C–O) and 1420 ν_{sym}(C–O) cm^{-1}. The Δ value ($\nu_{as}-\nu_{sym}$) indicates that the acetate anions

Table 1. Crystal data and structure refinement for $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$.

Complex	$[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$
Empirical formula	$C_{24}H_{16}CdN_6O_{4.35}$
Molecular weight	570.47
Temperature (K)	193
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.181(2)
b (Å)	10.277(2)
c (Å)	13.062(2)
α (°)	77.240(10)
β (°)	78.740(10)
γ(°)	70.080(10)
V (Å^3)	1120.4(4)
Z	2
D_{calcd}(g cm^{-3})	1.691
μ(mm^{-1})	1.022
F (000)	570
Crystal size (mm^3)	0.38 × 0.37 × 0.34
Index ranges	$-10 \leq h \leq 11$ $-12 \leq k \leq 12$ $-15 \leq l \leq 15$
Reflections collected	7485
Independent reflections (R_{int})	3941 (0.0252)
Reflections observed ($>2\sigma$)	3760
Completeness to theta	93.3%
Absorption correction	Numerical
Max. and min. transmissions	0.66 and 0.78
Data/Restraints/Parameters	3941/0/320
Goodness-of-fit on F^2	1.231
R [$I > 2\sigma$ (I)]	$R_1 = 0.0250$, $wR_2 = 0.0648$
R (all data)	$R_1 = 0.0282$, $wR_2 = 0.0799$
Largest difference peak and hole (e Å^{-3})	0.404 and −0.626

chelate to the M^{II} centre [13, 14]. Attempts to isolate a new nitrite and nitrate mixed-anion cadmium(II) complex of 1,10-phenanthroline (phen), $Cd(phen)_2(NO_2)(NO_3)$, were not successful, and $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$ was isolated. The IR spectra of this complex show $\nu(NO_2)$ and $\nu(NO_3)$ at *c*. 1232 and 1370 cm^{-1}, respectively. The structure of $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$ was confirmed by X-ray crystallography.

3.2. *Crystal structure of* $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$

An ORTEP drawing of $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$ is shown in figure 1, while selected bond distances and angles are listed in table 2. Single X-ray crystal analysis reveals that $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$ crystallizes in the triclinic space group P-1. The coordination number of this complex is unusual with the Cd atom coordinated by eight donors from three different ligands (four nitrogen atoms of the two 1,10-phenanthroline and four oxygen atoms of the nitrite and nitrate ligands); the resulting geometry around the Cd atom is distorted tricapped trigonal prismatic. The Cd–N distances are 2.406(3), 2.412(3), 2.424(2) and 2.481(3) Å, and also the Cd–O distances are 2.391(3), 2.448(3), 2.454(2) and 2.516(2) Å. The reported cadmium(II) complexes containing 1,10-phenanthroline [15, 16] are almost isostructure to the present one. In $[Cd(phen)_2(N_3)_2]$ and $[Cd(phen)_2Cl_2]$ like in $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$, two 'phen' ligands are cis, while they are trans in $[Cd(phen)_2(NO_3)_2]$.

The crystal contains nitrite and nitrate, with two independent NO_2^- anions in the structure, one coordinating the Cd atom via two oxygen atoms and the other crystallographically independent NO_2^- anion disordered sharing one position in the crystal with NO_3^-. Final refinement showed that 35% of these positions in the crystal are occupied by NO_3^- and 65% of positions contain NO_2^-.

The compound is packed in layers that are held together by normal van der Waals interactions. Within the layers, the packing of the complex is characterized by π–π stacking interactions [17, 18] between 'phen' rings of adjacent chains, as shown in figure 2 and two rings of each ligand overlapping. The main molecular planes are close to parallel and separated by a distance of ~3.5 Å, resembling the planes in graphite. Parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the 'π-stacking' type, rather than 'edge-to-face' or 'vertex-to-face' types [19, 20]. Projection of the structure perpendicular to the ring plane shows the overall form of 'slipped' stacking, which is at least qualitatively understandable in terms of optimizing approaches between atoms of opposite charges. Such a parallel-displaced structure also has a contribution from π–σ attraction, greater with increasing offset. In the crystal reported here, the interplanar distance is 3.53 Å, a normal π–π stacking [21–23].

Electron-poor aromatic groups interact most strongly with electron-rich aromatic groups [22]. Hence, it can be expected that in $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$, interaction of the electron-poor pyridyl rings with less electron-poor phenyl groups should be favoured.

Supplementary material

Crystallographic data for the structure reported in the article have been deposited with the Cambridge Crystallographic Data Centre as supplementary

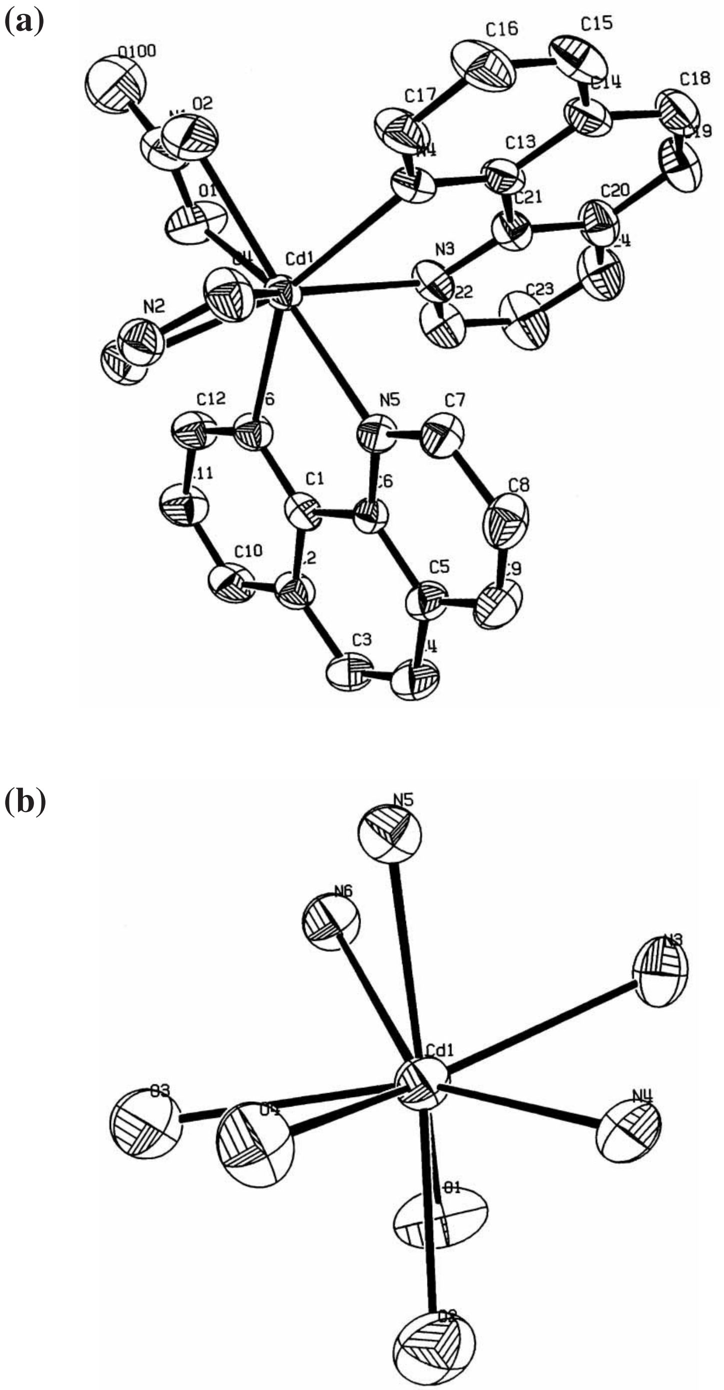

Figure 1. (a) ORTEP diagram of the [Cd(phen)$_2$(NO$_2$)$_{1.65}$(NO$_3$)$_{0.35}$] with ellipsoids 50% probability. (b) Coordination polyhedron in the [Cd(phen)$_2$(NO$_2$)$_{1.65}$(NO$_3$)$_{0.35}$].

Table 2. Bond lengths (Å) and angles (°) for $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$.

Cd1–O1	2.391(3)	Cd1–O2	2.448(3)
Cd1–N4	2.406(3)	Cd1–O3	2.454(2)
Cd1–N5	2.412(3)	Cd1–N3	2.481(3)
Cd1–N6	2.424(2)	Cd1–O4	2.516(2)
O1–Cd1–N6	80.87(9)	O1–Cd1–O3	94.82(10)
N4–Cd1–N6	145.41(9)	N4–Cd1–O3	126.78(8)
N5–Cd1–N6	68.32(9)	N5–Cd1–O3	88.39(9)
N5–Cd1–N6	68.32(9)	N6–Cd1–O3	79.33(8)
O1–Cd1–O2	51.91(9)	O2–Cd1–O3	84.86(9)
N4–Cd1–O2	80.76(9)	O1–Cd1–N3	88.15(10)
N5–Cd1–O2	159.87(9)	N4–Cd1–N3	67.55(9)
N5–Cd1–N3	79.51(9)	N5–Cd1–O4	78.04(9)
N6–Cd1–N3	82.91(9)	N6–Cd1–O4	119.08(8)
O2–Cd1–N3	111.13(10)	O2–Cd1–O4	83.15(10)
N6–Cd1–O2	128.49(9)	O3–Cd1–O4	49.74(8)
N3–Cd1–O4	138.85(8)		

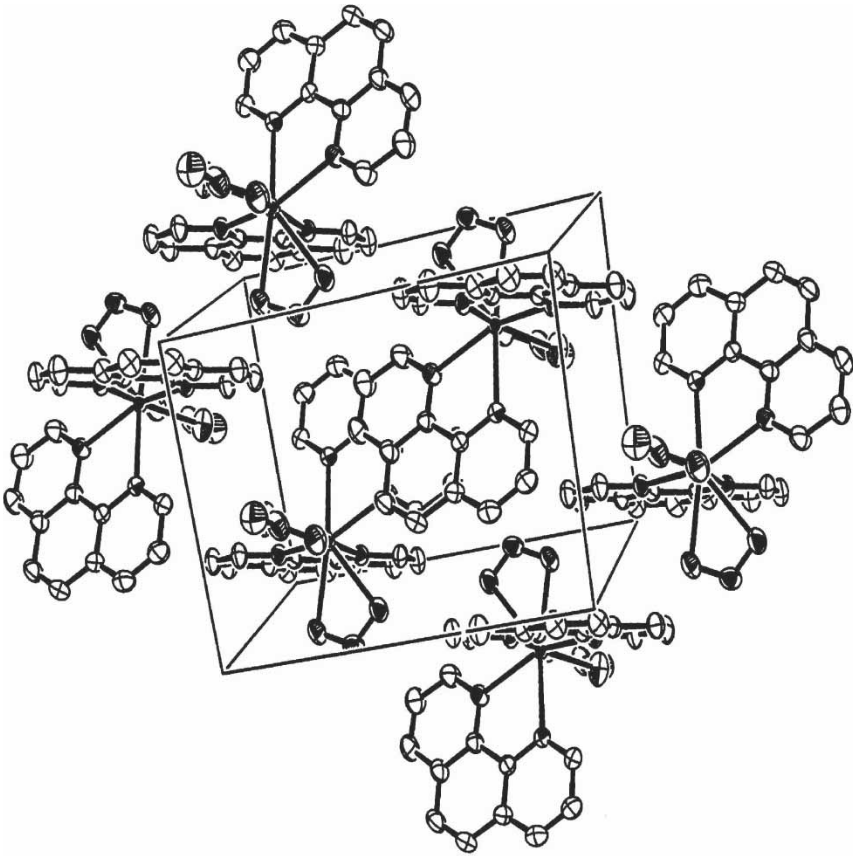

Figure 2. Unit cell showing the π–π stacking interaction (charge-transfer arrays) between the parallel aromatic rings in $[Cd(phen)_2(NO_2)_{1.65}(NO_3)_{0.35}]$.

publication no, CCDC-249986. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk).

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