

Hacali Necefoğlu,^a Tuncer Hökelek,^{b*} Cem Cüneyt Ersanlı^c and Ahmet Erdönmez^c

^aKafkas University, Department of Chemistry, 63100, Kars, Turkey, ^bHacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and ^cOndokuzmayıs University, Department of Physics, 55132 Kurupelit, Samsun, Turkey

Correspondence e-mail: merzifon@hacettepe.edu.tr

Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.033

wR factor = 0.095

Data-to-parameter ratio = 11.6

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

Bis(4-hydroxybenzoato- κO)bis(nicotinamide- κN)zinc(II)

The title compound, $[\text{Zn}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{C}_7\text{H}_5\text{O}_3)_2]$, crystallizes as mononuclear molecules with distorted trigonal-bipyramidal zinc coordination. One of the 4-hydroxybenzoate ions is coordinated to zinc as a bidentate ligand, while the other is monodentate. Intermolecular hydrogen bonds between nicotinamide N and carboxyl O atoms, as well as between the nicotinamide O and hydroxybenzoate O atoms, support the molecular packing. Hydrogen bonding of the carboxylate O atoms has an effect on the delocalization in the carboxylate groups.

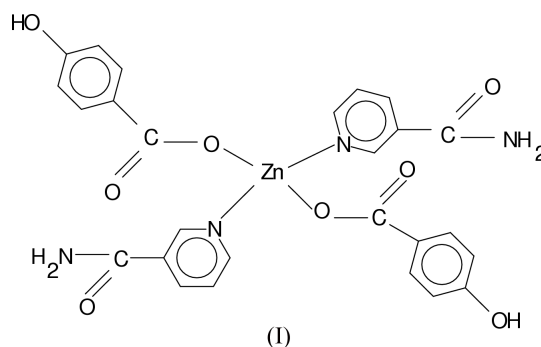
Received 20 November 2002

Accepted 22 November 2002

Online 30 November 2002

Comment

Nicotinamide (NA) is one form of niacin. A deficiency of this vitamin leads to loss of copper from the body, known as pellagra disease. Victims of pellagra show unusually high serum and urinary copper levels (Krishnamachari, 1974). The nicotinic acid derivative *N,N*-diethylnicotinamide (DENA) is an important respiratory stimulant (Bigoli *et al.*, 1972).



The structures of some complexes obtained from the reactions of transition metal(II) ions with different benzoic and/or nicotinic acid derivatives as ligands have been the subject of much interest in our laboratory; examples are $[\text{Zn}(\text{C}_7\text{H}_5\text{O}_3)(\text{OH}_2)_3(\text{NA})] \cdot \text{C}_7\text{H}_5\text{O}_3\text{H}_5$ [(II); Hökelek & Necefoğlu, 2001], $[\text{Co}(\text{C}_7\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})_2(\text{NA})_2]$ [(III); Hökelek & Necefoğlu, 1999a], $[\text{Co}(\text{C}_7\text{H}_5\text{O}_2)_2(\text{NA})_2(\text{H}_2\text{O})_2]$ [(IV); Hökelek & Necefoğlu, 1999b], $[\text{Co}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{NA})_2(\text{H}_2\text{O})_2]$ [(V); Hökelek & Necefoğlu, 1999c], $[\text{Cu}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{NA})_2(\text{H}_2\text{O})_2]$ [(VI); Hökelek, Budak *et al.*, 1998], $[\text{Cu}_3\{(\text{NO}_2)_2\text{C}_6\text{H}_3\text{COO}\}_6(\text{CH}_3\text{OH})_2]_n$ [(VII); Hökelek, Mert, & Ünaleroğlu, 1998], $[\text{Co}(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{NA})_2(\text{H}_2\text{O})_2]$ [(VIII); Hökelek & Necefoğlu, 1998], $[\text{Cu}(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{DENA})_2(\text{H}_2\text{O})_2]$ [(IX); Hökelek *et al.*, 1997], $[\text{Co}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{DENA})_2(\text{H}_2\text{O})_2]$ [(X); Hökelek & Necefoğlu, 1997], $[\text{Zn}_2(\text{C}_7\text{H}_5\text{O}_3)_4(\text{DENA})_2(\text{H}_2\text{O})_2]$ [(XI); Hökelek & Necefoğlu, 1996],

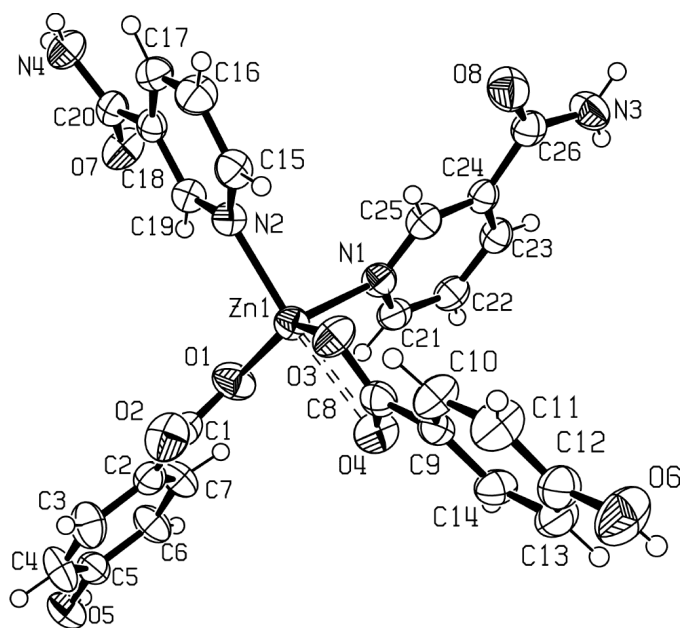


Figure 1

An ORTEP-3 (Farrugia, 1997) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

[Cu(C₇H₅O₂)₂(DENA)₂] [(XII); Hökelek *et al.*, 1996] and [Cu₂(C₆H₅COO)₄(DENA)₂] [(XIII); Hökelek *et al.*, 1995]. In (XIII), the benzoate ion acts as a bidentate ligand, but in (XI) two of the benzoate ions acts as monodentate ligands, while the other two are bidentate, bridging the two Zn atoms.

The solid-state structures of anhydrous zinc(II) carboxylates include one-dimensional (Guseinov *et al.*, 1984; Clegg *et al.*, 1986a), two-dimensional (Clegg *et al.*, 1986b, 1987) and three-dimensional (Capilla & Aranda, 1979) polymeric motifs of different types, while discrete monomeric complexes with octahedral and tetrahedral coordination geometry are found if water or other donor molecules are coordinated to Zn (van Niekerk *et al.*, 1953; Usabaliev *et al.*, 1992). In hexaaquazinc(II) bis(4-hydroxybenzoate) dihydrate, [Zn(H₂O)₆](4-HOC₆H₄COO)₂·2H₂O, which is isostructural with the corresponding Mg^{II}, Co^{II}, Ni^{II} and Mn^{II} compounds, the carboxylate ion lies outside the coordination sphere of the Zn atom (Musaev *et al.*, 1983), while [Zn(4-HOC₆H₄COO)₂]₂·4C₅H₅N forms a clathrate, consisting of [Zn(4-HOC₆H₄COO)₂(C₅H₅N)₂] units with tetrahedral coordination geometry and free pyridine molecules (Nadzhafov *et al.*, 1981).

The structure determination of the title compound, (I), a zinc complex with two NA and two 4-hydroxybenzoate ligands, was undertaken in order to determine the ligand properties of (NA) and 4-hydroxybenzoate ligands and also to compare the results obtained with those reported previously. In the monomeric title complex, [Zn(C₇O₃H₅)₂(NA)₂], the Zn atom is surrounded by two NA and two 4-hydroxybenzoate ligands. One of the 4-hydroxybenzoate ions acts as a bidentate ligand, while the other and two NA are monodentate ligands.

A view of the molecule with the atomic numbering scheme is shown in Fig. 1.

Although the Zn atom has four-coordination, close contact of the O4 atom [Zn1···O4 = 2.404 (2) Å] may be considered to give five-coordination; this distance is much greater than the sum of the corresponding ionic radii (2.14 Å; Day & Selbin, 1969). Similar reported Zn···O contacts are 2.50 (1) Å in [Zn(*n*-HOC₆H₄COO)₂(C₅H₅N)₂]₂·2C₅H₅N (Nadzhafov *et al.*, 1981) and 2.494 (8) Å in [Zn(*p*-H₂NC₆H₄COO)₂]_n·1.5nH₂O (Amiraslanov *et al.*, 1980). The five-coordination around Zn^{II} can be described as a distorted trigonal bipyramid or a distorted square pyramid. Further information can be obtained by estimating the structural index τ (Uhlenbrock *et al.*, 1996), which represents the relative amount of trigonality [square pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$; $\tau = (\beta - \alpha)/60^\circ$, α and β being the two largest angles around the central atom]. The value of τ is 0.36 for (I) [$\alpha = 138.00$ (7) and $\beta = 159.61$ (6) °]. The coordination of the Zn^{II} atom is therefore best described as a distorted trigonal bipyramid.

In the binuclear complex (XI), the average Zn—O bond length [1.953 (2) Å] is shorter than the corresponding value in (I) [2.107 (2) Å], but Zn is four-coordinate. The average Zn—N bond length [2.075 (2) Å] in (I) is in good agreement with the values reported for tetrahedrally coordinated Zn complexes [2.006 (5) Å in Zn₂(DENA)₂(NCS)₄ (Bigoli *et al.*, 1973a), 2.054 (6) and 2.055 (6) Å in ZnCl₂(DENA)₂ (Khodashova *et al.*, 1978), and 2.068 (7) Å in ZnI₂(DENA)₂ (Sergienko *et al.*, 1978)], while it is shorter than the corresponding value in the octahedrally coordinated zinc complex [Zn(DENA)₂(NCS)₂]₂·2H₂O [2.171 (4) Å; Bigoli *et al.*, 1973b]. The aromatic bonds C5—O5 [1.365 (3) Å] and C12—O6 [1.359 (3) Å] are in agreement with the corresponding values for 4-hydroxybenzoic acid monohydrate (Colapietro *et al.*, 1979).

The N1—Zn1···O4 and O3—Zn1···O4 angles are 88.86 (7) and 58.79 (6)°, respectively. The corresponding N—M···O and O—M···O (where M is a metal atom) angles are 90.4 (4) and 58.3 (3)° in (XI) (Hökelek *et al.*, 1996), and 89.6 (1), 89.0 (1) and 55.2 (1)° in [Cu(Asp)₂(py)₂] (where Asp is acetylsalicylate and py is pyridine) (Greenaway *et al.*, 1984). The Zn1 atom lies −0.1931 (2) and 0.2208 (2) Å out of the O1/C1/O2 and O3/C8/O4 carboxyl planes, respectively.

In the carboxylate group, the C1—O1 and C8—O3 bond lengths [1.281 (3) and 1.274 (3) Å] are a little larger than the C1—O2 and C8—O4 [1.240 (3) and 1.245 (3) Å] bond lengths and may be compared with the corresponding distances in the monomeric and dimeric carboxylate pyridine complexes: 1.266 (5) and 1.248 (6) Å in (III), 1.255 (1) and 1.253 (2) Å in (IV), 1.263 (5) and 1.258 (6) Å in (V), 1.278 (3) and 1.246 (3) Å in (VI), 1.254 (2) and 1.251 (2) Å in (VIII), 1.267 (6) and 1.237 (4) Å in (IX), 1.251 (6) and 1.254 (7) Å in (X), 1.279 (4) and 1.246 (4) Å in (XI), and 1.277 (4) and 1.239 (4) Å in (XII).

One of the carboxylates is bidentate, while the other is monodentate, but the near equality of the two C—O bond lengths in each carboxylate groups (Table 1) indicates a delocalized bonding arrangement, rather than localized single

and double bonds. This may be due to the intermolecular hydrogen bonds of the carboxyl O atoms (Table 2).

The dihedral angles between the mean planes of the carboxyl groups (O1/C1/O2 and O3/C8/O4) and the phenyl rings [*A* (C2–C7) and *B* (C9–C14)] in the hydroxybenzoate anions are 12.2 (2) and 10.0 (2)°, respectively; these may be compared with the corresponding values of 24.1 (4)° in (III), 13.0 (2)° in (IV), 14.2 (3)° in (V), 23.7 (3)° in (VIII), 10.2 (7)° in (IX), 2.2 (6)° in (X), 17.9 (7) and 136.1 (2)° in (XI), and 6.7 (9)° in (XII). The configuration around the Zn1 atom is given by the torsion angles listed in Table 1.

There are intermolecular hydrogen bonds between nicotinamide N atoms and carboxyl O atoms, as well as between the nicotinamide O atoms and hydroxybenzoate O atoms of neighbouring molecules (Table 2). These intermolecular hydrogen bonds, together with dipole–dipole and van der Waals interactions, support the molecular packing.

All rings are essentially planar, with maximum deviations of 0.011 (2) Å for C7 and 0.011 (2) Å for C21. The rings are twisted with respect to each other; dihedral angles between least-squares planes are *A/B* = 79.36 (7), *A/C* = 84.50 (8), *A/D* = 12.62 (8), *B/C* = 20.39 (7), *B/D* = 77.28 (6) and *C/D* = 89.57 (7)°.

Experimental

The title compound, (I), was prepared by the reaction of 0.02 mol of NA in H₂O (50 ml), 0.01 mol of ZnSO₄ in H₂O (100 ml), and 0.02 mol of sodium *p*-hydroxybenzoate in H₂O (100 ml). The mixture was filtered and set aside to crystallize at ambient temperature for several days, giving colourless single crystals.

Crystal data

[Zn(C₆H₆N₂O)₂(C₇H₅O₃)₂]
M_r = 583.85
 Monoclinic, *P*2₁/*n*
a = 10.3159 (10) Å
b = 22.606 (3) Å
c = 10.8926 (10) Å
 β = 95.375 (6)°
V = 2529.0 (5) Å³
Z = 4

D_x = 1.533 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 10–18°
 μ = 1.03 mm⁻¹
T = 293 (2) K
 Rod, colourless
 0.30 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius TurboCAD4 diffractometer
 Non-profiled ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.748, *T_{max}* = 0.861
 5409 measured reflections
 5124 independent reflections
 4089 reflections with *I* > 2σ(*I*)

R_{int} = 0.031
 θ_{\max} = 26.3°
h = -12 → 0
k = -28 → 0
l = -13 → 13
 3 standard reflections
 frequency: 120 min
 intensity decay: 1%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.033
wR(*F*²) = 0.095
S = 1.05
 5124 reflections
 440 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.716P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.29 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.49 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Zn1–O1	1.9295 (16)	O8–C26	1.232 (3)
Zn1–O3	1.9883 (16)	C8–O4	1.245 (3)
Zn1–N1	2.0723 (18)	C5–O5	1.365 (3)
Zn1–N2	2.0784 (17)	N3–C26	1.329 (3)
Zn1–O4	2.4042 (18)	O7–C20	1.232 (3)
O3–C8	1.274 (3)	N4–C20	1.328 (3)
O2–C1	1.240 (3)	C12–O6	1.359 (3)
O1–C1	1.281 (3)		
O1–Zn1–O3	138.00 (7)	O3–Zn1–O4	58.79 (6)
O1–Zn1–N1	102.07 (8)	N1–Zn1–O4	88.86 (7)
O3–Zn1–N1	108.05 (7)	N2–Zn1–O4	159.61 (6)
O1–Zn1–N2	103.94 (7)	O2–C1–O1	123.5 (2)
O3–Zn1–N2	100.91 (7)	O4–C8–O3	120.4 (2)
N1–Zn1–N2	96.70 (7)	O8–C26–N3	122.3 (2)
O1–Zn1–O4	93.97 (7)	O7–C20–N4	122.0 (2)
O1–Zn1–O3–C8	59.86 (18)	O3–Zn1–N2–C15	11.05 (18)
N1–Zn1–O3–C8	-73.82 (15)	N1–Zn1–N2–C15	-98.85 (17)
N2–Zn1–O3–C8	-174.65 (13)	O4–Zn1–N2–C15	6.2 (3)
O1–Zn1–N2–C19	-28.41 (17)	O3–Zn1–O1–C1	29.4 (2)
N1–Zn1–N2–C19	75.84 (16)	N1–Zn1–O1–C1	164.68 (16)
O4–Zn1–N2–C19	-179.15 (16)	N2–Zn1–O1–C1	-95.18 (16)
O1–Zn1–N2–C15	156.90 (16)	O4–Zn1–O1–C1	74.99 (17)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O6–H6A...O8 ⁱ	0.74 (5)	2.03 (5)	2.764 (3)	175 (6)
O5–H5A...O7 ⁱⁱ	0.83 (4)	1.91 (4)	2.735 (3)	175 (4)
N3–H3B...O4 ⁱⁱⁱ	0.89 (3)	2.04 (3)	2.872 (3)	155 (3)
N4–H4A...O2 ^{iv}	0.83 (3)	2.26 (3)	3.084 (3)	171 (3)

Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (iv) 1 - *x*, 2 - *y*, 2 - *z*.

H atoms were located in a difference map and refined isotropically.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors acknowledge the purchase of the CAD-4 diffractometer under grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

References

- Amiraslanov, I. R., Nadzhafov, G. N., Usubaliyev, B. T., Musaev, A. A., Movsumov, E. M. & Mamedov, Kh. S. (1980). *Zh. Strukt. Khim.* **21**, 140–145.
 Bigoli, F., Braibanti, A., Pellinghelli, M. A. & Tiripicchio, A. (1972). *Acta Cryst.* **B28**, 962–966.
 Bigoli, F., Braibanti, A., Pellinghelli, M. A. & Tiripicchio, A. (1973a). *Acta Cryst.* **B29**, 2708–2712.
 Bigoli, F., Braibanti, A., Pellinghelli, M. A. & Tiripicchio, A. (1973b). *Acta Cryst.* **B29**, 2344–2348.
 Capilla, A. V. & Aranda, R. A. (1979). *Cryst. Struct. Commun.* p. 8, 795–798.
 Clegg, W., Little, I. R. & Straughan, B. P. (1986a). *Acta Cryst.* **C42**, 919–920.
 Clegg, W., Little, I. R. & Straughan, B. P. (1986b). *Acta Cryst.* **C42**, 1701–1703.
 Clegg, W., Little, I. R. & Straughan, B. P. (1987). *Acta Cryst.* **C43**, 456–457.

- Colapietro, M., Domenicano, A. & Marciante, C. (1979). *Acta Cryst.* **B35**, 2177–2180.
- Day, M. C. & Selbin, J. (1969). *Theoretical Inorganic Chemistry*, p. 109. New York: Van Nostrand Reinhold.
- Guseinov, G. A., Musaev, F. N., Usubaliyev, B. T., Amiraslanov, I. R. & Mamedov, Kh. S. (1984). *Koord. Khim.* **10**, 117–122.
- Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Greenaway, F. T., Pezeshk, A., Cordes, A. W., Noble, M. C. & Sorenson, J. R. J. (1984). *Inorg. Chim. Acta*, **93**, 67–71.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Hökelek, T., Budak, K. & Necefoğlu, H. (1997). *Acta Cryst.* **C53**, 1049–1051.
- Hökelek, T., Budak, K., Sendil, K. & Necefoğlu, H. (1998). *Acta Cryst.* **C54**, 347–348.
- Hökelek, T., Gündüz, H. & Necefoğlu, H. (1996). *Acta Cryst.* **C52**, 2470–2473.
- Hökelek, T., Mert, Y. & Ünaleroğlu, C. (1998). *Acta Cryst.* **C54**, 310–313.
- Hökelek, T. & Necefoğlu, H. (1996). *Acta Cryst.* **C52**, 1128–1131.
- Hökelek, T. & Necefoğlu, H. (1997). *Acta Cryst.* **C53**, 187–189.
- Hökelek, T. & Necefoğlu, H. (1998). *Acta Cryst.* **C54**, 1242–1244.
- Hökelek, T. & Necefoğlu, H. (1999a). *Anal. Sci.* **15**, 1043–1044.
- Hökelek, T. & Necefoğlu, H. (1999b). *Acta Cryst.* **C55**, 545–547.
- Hökelek, T. & Necefoğlu, H. (1999c). *Acta Cryst.* **C55**, 1438–1440.
- Hökelek, T. & Necefoğlu, H. (2001). *Anal. Sci.* **17**, 1241–1242.
- Hökelek, T., Necefoğlu, H. & Balci, M. (1995). *Acta Cryst.* **C51**, 2020–2023.
- Khodashova, T. S., Poray-Koshits, M. A., Rubinchik, B. Ya., Butman, L. A. & Tsintsadze, G. V. (1978). *Koord. Khim.* **4**, 1753–1759.
- Krishnamachari, K. A. V. R. (1974). *Am. J. Clin. Nutr.* **27**, 108–111.
- Musaev, F. N., Nadzhafov, G. N. & Mamedov, Kh. S. (1983). *Koord. Khim.* **12**, 37–46.
- Nadzhafov, G. N., Usubaliyev, B. T., Amiraslanov, I. R., Movsumov, E. M. & Mamedov, Kh. S. (1981). *Koord. Khim.* **7**, 770–775.
- Niekerk, J. N. van, Schoening, F. R. L. & Talbot, J. H. (1953). *Acta Cryst.* **6**, 720–723.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sergienko, V. S., Poray-Koshits, M. A., Rubinchik, B. Ya., Butman, L. A. & Tsintsadze, G. V. (1978). *Koord. Khim.* **4**, 1760–1764.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Uhlenbrock, S., Wegner, R. & Krebs, B. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3731–3736.
- Usubaliyev, B. T., Guliev, F. I., Musaev, F. N., Ganbarov, D. M., Ashurova, S. A. & Movsumov, E. M. (1992). *Zh. Strukt. Khim.* **33**, 203–207.