



Synthesis and characterization of a potassium complex of magneson: $[K(HL)(OH_2)_2]_\infty$ [$H_2L = 4-(4\text{-nitrophenylazo})\text{resorcinol (magneson)}$]

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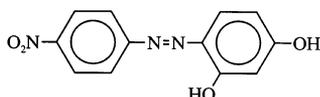
Abstract

The synthesis and crystallographic, spectroscopic and thermal characterization of the potassium complex $[K(HL)(OH_2)_2]_\infty$ [$H_2L = 4-(4\text{-nitrophenylazo})\text{resorcinol (magneson)}$] are reported. In the solid state, the K^+ ion is heptacoordinated and the ligand binds with three different coordination modes (via a bidentate chelating nitro group, a bridging nitro oxygen and a phenolic oxygen), giving rise to a polymeric structure. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

o-Hydroxydiaryldazo compounds are very weak acids that exist in solution as an equilibrium mixture of strongly hydrogen-bonded azo and hydrazone forms. They have been used in dyestuffs, as spectrophotometric and titrimetric reagents, and in solvent extraction studies [1]. Although their hard donor atoms are eminently suitable for coordination to alkali metals, little is known of such complexes, especially as regards the coordination environment of the metal (possibly because crystallographic studies are required, alkali metals commonly being spectroscopically silent). This is



Scheme 1.

a subject of potential interest because of the possibility of organometallic polymer formation presented by *o*-hydroxydiaryldazo ligands that, as well as the azo nitrogens and the *ortho* oxygen, also have donor atoms in other parts of the molecule. Coordination polymers can exhibit properties including electrical conductivity or magnetism [2,3], and can also be of potential use for catalysis [4].

In the course of a study of the solid state structures and properties of metal complexes of *o*-hydroxydiaryldazo compounds, we have synthesized the potassium(I) complex of the azo dye magneson [4-(*p*-nitrophenylazo)resorcinol, H_2L ; Scheme 1]. Here we report its synthesis, its IR, electronic and 1H NMR spectra, and its structure as determined by X-ray diffractometry.

2. Experimental

2.1. Methods and materials

All chemicals were of reagent grade and were used without further purification. 1H NMR data for mag-

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Table 1
Crystal data and structure refinement for $[K(HL)(OH_2)_2]_{\infty}$

Empirical formula	$C_{12}H_{12}N_3O_6K$
Formula weight	333.35
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
Unit cell dimensions	
a (Å)	6.961(1)
b (Å)	7.775(2)
c (Å)	26.597(4)
β (°)	96.214(16)
V (Å ³)	1431.0(4)
Z	4
D_{calc} (Mg cm ⁻³)	1.547
Absorption coefficient (mm ⁻¹)	0.405
$F(000)$	688
Crystal size (mm)	0.20 × 0.20 × 0.10
θ Range (°)	2.73–23.68
Index ranges	–7/7, –8/0, 0/30
Reflections collected	2209
Independent reflections	2156 [$R_{\text{int}} = 0.1154$]
Max/min transmission	0.963/0.935
Data/parameters	2156/205
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.053$, $wR_2 = 0.117$
R indices (all data)	$R_1 = 0.287$, $wR_2 = 0.169$
Extinction coefficient	0.0037(12)
Goodness-of-fit on F^2	0.947
Largest diff. peak and hole (e Å ⁻³)	0.302/–0.312

neson (DMSO- d_6 , ppm): 6.28 (d, 1H, C(3)–H), 6.45 (dd, 1H, C(5)–H), 7.61 (d, 1H, C(6)–H), 7.99 (d, 2H, C(22,26)–H), 8.32 (d, 2H, C(23,25)–H).

Elemental analysis was performed on a FISON S EA-1108 elemental analyzer. The melting point of the new complex was measured in a Büchi melting point apparatus and is uncorrected. Its IR spectrum in the region 400–4000 cm⁻¹ was recorded using KBr pellets on a Bruker VECTOR 22 spectrophotometer, its solid state electronic spectrum (250–900 nm) on a Shimadzu UV-3101PC spectrophotometer, its electronic spectrum in solution (300–800 nm) with a CECIL CE 2021 spectrophotometer and its ¹H NMR spectrum on a Bruker AMX400 instrument using TMS as reference. TG/DTG thermal analysis (pyrolysis, 300–1000 K) was performed in a 100 ml min⁻¹ current of air using a Shimadzu TGA-DTG-50H thermobalance coupled to a Nicolet Magma 550 IR-FT spectrometer and a Fisons Thermolab mass spectrometer for identification of evolved gases.

2.2. Preparation of $[K(HL)(OH_2)_2]_{\infty}$

Procedure (a). A solution of NiCl₂·6H₂O (0.78 mmol) in methanol was added to a suspension of H₂L (0.78 mmol) and 1,1'-bis-2-naphthol (0.78 mmol) in 20 ml of the same solvent. The mixture was refluxed for 2 h, a solution of KOH (2.51 mmol) in MeOH (10 ml) was slowly added, and reflux was continued for 1.5 h. Slow evaporation of the solvent at room temperature (r.t.)

afforded, after a few days, well-shaped prismatic brown crystals that were suitable for diffractometric structure analysis.

Procedure (b). A 0.15 M aqueous solution of KOH (1.45 ml) was added to a suspension of H₂L (0.20 mmol) in 15 ml of EtOH. The mixture was refluxed for 1 h and stirred at r.t. for a week. The brown precipitate obtained upon slow evaporation of the solvents in air was filtered out. Yield: 45%; m.p. > 250 °C.

Analytical and spectroscopic data of the complex. *Anal.* Found: C, 42.9; H, 3.4; N, 12.6. Calc. for C₁₂H₁₂N₃O₆K: C, 43.2; H, 3.6; N, 12.6%. Selected IR data (KBr pellets, cm⁻¹): 3420 sh, ν (OH); 3265 b, ν (NH); 1685 m, ν (CO); 1555 m, ν (C=N); 942 m, ν (NOH).

¹H NMR (DMSO- d_6 , ppm): 5.10 (d, 1H, C(3)–H), 5.91 (dd, 1H, C(5)–H), 6.74 (d, 1H, C(6)–H), 7.31 (d, 2H, C(22,26)–H), 8.10 (d, 2H, C(23,25)–H).

2.3. X-ray crystallography

A single brown prismatic crystal was mounted on an Enraf–Nonius MACH3 diffractometer and data were collected by the ω scan technique at r.t. using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) [5]. The unit cell dimensions were obtained from a least-squares fit to the setting angles of 25 reflections. Lorentz, polarization and Ψ -scan absorption corrections were applied [6]. Crystal data are listed in Table 1.

The structure was solved using the heavy atom method [7] and refined on F^2 by full-matrix least-squares techniques with anisotropic displacement factors for all non-hydrogen atoms [8]. The positions of most H atoms were calculated geometrically and included in structure factor calculations, but the H atoms of the water molecules and the H atoms located on the N_{hydrazo} atom (see below) were located in difference maps and their positions were refined isotropically. An extinction correction was also refined. The high value of final parameter R for all data can be derived from scanning effects along the z -axis. Molecular graphics were obtained using SCHAKAL [9] and ZORTEP [10].

3. Results and discussion

Crystals of $[K(HL)(OH_2)_2]_{\infty}$ suitable for structure analysis by X-ray diffractometry were obtained by slow evaporation in air, of a methanolic solution containing NiCl₂·6H₂O, H₂L, 1,1'-bis-2-naphthol and KOH in 1:1:1:3.2 mole ratio. Reaction of H₂L with KOH in EtOH afforded the same compound as a powder. The new compound is only sparingly soluble in water, methanol, ethanol and most other solvents, but is moderately soluble in acetone and in DMSO.

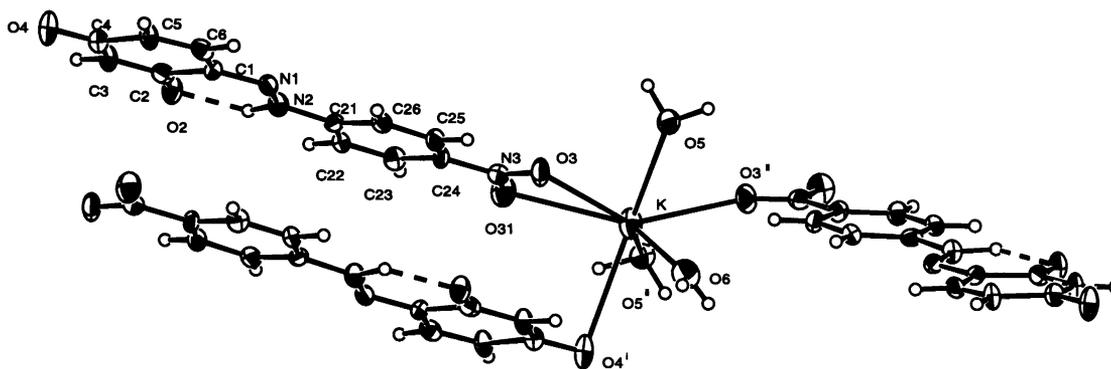


Fig. 1. ORTEP plot of the coordination environment of the potassium atom (i: $x + 1, y + 1/2, -z - 1/2$; ii: $x + 1, -y + 2, -z$). Thermal ellipsoids are shown at the 30% probability level.

3.1. Crystal structure

A plot of $[K(HL)(OH_2)_2]_\infty$ showing the immediate coordination environment around the central metal ion is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2.

The asymmetric unit consists of a potassium ion, one HL^- anion and two water molecules. The potassium ion is heptacoordinated to the oxygens of three water molecules [$O5, O5^i$ and $O6$ (i: $-x + 1, y + 1/2, -z - 1/2$)] and to three HL^- anions, of which one coordinates via the deprotonated *p*-hydroxy group of its resorcinol moiety, one through one of its nitro oxygens, and the third through both these oxygens, forming a four-membered chelate ring (Fig. 1). The eighth nearest neighbor of the K atom, $N3$, lies $3.390(7)$ Å away, farther than the 3.2 Å normally considered as the limiting distance for significant interaction with potassium [11]. The coordination polyhedron is very irregular, but might be described as a heavily distorted pentagonal bipyramid with an axial O–K–O angle of $149.49(15)^\circ$ defined by the water oxygen $O5$ and the hydroxyl oxygen $O4^{ii}$ (ii: $-x + 1, -y + 2, -z$); the narrowest of the angles between adjacent equatorial atoms is the O–K–O angle of the chelate ring, $42.31(14)^\circ$.

The shortest coordinating bond lengths are those of the K– O_{water} bonds, 2.688 – 2.836 Å. Two of these oxygens, $O5$ and $O5^i$, bridge to neighboring metal atoms, the K–K distance being 4.3154 Å (Fig. 2). The K– O_{nitro} distances [$K-O3 = 2.974(5)$ Å, $K-O31 = 3.018(5)$ Å, $K-O3^i = 2.884(6)$ Å] are within the usual range for nitro-compounds of potassium [12,13]. Those involved in the chelate ring are quite similar, making the ring almost symmetrical, whereas the K–O–K bridge formed by $O3^i$ (Fig. 2) is quite asymmetrical, the bond that does not form part of a chelate ring being significantly shorter than the other. The K– O_{Ph} bond K– $O4^{ii}$ is relatively weak, with a length of $3.116(6)$ Å.

The essentially planar ligand is coordinated in the hydrazone form; the position of the hydrogen atom $H02$ successfully refined to a location on $N2$ (where it forms an intramolecular hydrogen bond with $O2$; see Table 3) and the $N1$ – $N2$ distance, $1.335(7)$ Å, is too long for a double bond. However, since $N1$ – $N2$ is also considerably shorter than the accepted length of single bonds (1.44 Å), and in view of the relatively short distances $C2$ – $O2$ ($1.301(8)$ Å) and $C4$ – $O4$ ($1.260(8)$ Å) and the intermediate length of $N1$ – $C1$ (Table 2), there must be extensive delocalization of negative charge (Scheme 2).

The potassium atoms are linked into chains along the *b*-axis by the oxygen bridges through $O3$ and $O5$, neighboring chains having opposite senses and being

Table 2
Selected bond lengths (Å) and bond angles ($^\circ$) in $[K(HL)(OH_2)_2]_\infty$

Bond lengths			
K–O6	2.688(8)	N1–N2	1.335(7)
K–O5 ⁱ	2.758(5)	N1–C1	1.327(8)
K–O5	2.836(5)	O2–C2	1.301(8)
K–O3 ⁱ	2.884(6)	O4–C4	1.260(8)
K–O3	2.974(5)	C1–C6	1.444(9)
K–O31	3.018(5)	C1–C2	1.469(9)
K–O4 ⁱⁱ	3.116(6)	C2–C3	1.383(9)
K–N3	3.390(7)	C3–C4	1.414(9)
		C4–C5	1.445(9)
		C5–C6	1.325(8)
Bond angles			
O6–K–O5 ⁱ	125.7(2)	O5 ⁱ –K–O31	96.19(16)
O6–K–O5	80.74(17)	O5–K–O31	97.33(16)
O5 ⁱ –K–O5	129.93(15)	O3 ⁱ –K–O31	145.89(17)
O6–K–O3 ⁱ	84.72(18)	O3–K–O31	42.31(14)
O5 ⁱ –K–O3 ⁱ	69.24(15)	O6–K–O4 ⁱⁱ	74.66(15)
O5–K–O3 ⁱ	72.83(15)	O5 ⁱ –K–O4 ⁱⁱ	79.77(14)
O6–K–O3	91.9(2)	O5–K–O4 ⁱⁱ	149.59(15)
O5 ⁱ –K–O3	138.28(16)	O3 ⁱ –K–O4 ⁱⁱ	121.42(15)
O5–K–O3	66.96(14)	O3–K–O4 ⁱⁱ	95.96(14)
O3 ⁱ –K–O3	139.66(11)	O31–K–O4 ⁱⁱ	83.69(15)
O6–K–O31	126.8(2)		

Symmetry transformations: (i) $x + 1, y + 1/2, -z - 1/2$; (ii) $-x + 1, -y + 2, -z$.

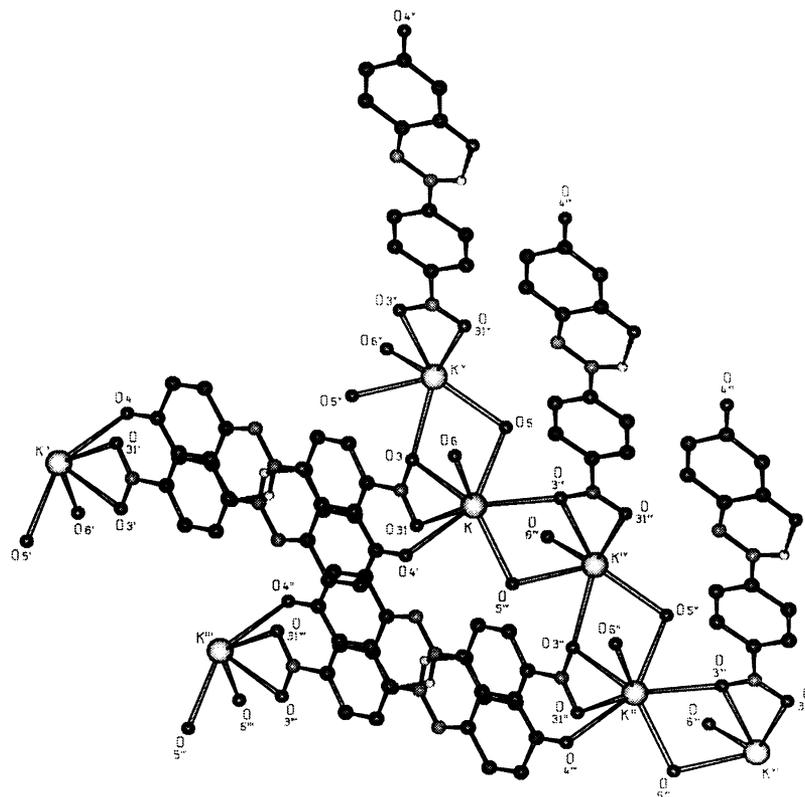


Fig. 2. Diagram depicting the zigzag chain of potassium atoms along the *b*-axis (hydrogen atoms omitted for clarity).

linked to each other by pairs of ligand anions, with alternate potassiums in each chain linking to the neighboring chains on opposite sides (Fig. 2). The two ligands in each K-chain-linking pair are parallel to each other, but the shortest centroid-to-centroid distance between rings of opposed ligands is 3.905 Å between the centroids of the rings C1–C2–C3–C4–C5–C6 and [C21–C22–C23–C24–C25–C26]ⁱⁱ [14], which is rather too long for π stacking [15]. The K–O4ⁱⁱ bonds (3.116 Å) are almost perpendicular to the ligand planes [K–O4ⁱⁱ–C4ⁱⁱ = 96.4(5)°, O3–K–O4ⁱⁱ = 95.96(14)°, O31–K–O4ⁱⁱ = 86.69(15)°], so that together with the K–O4 axes (of length 15.142 Å) they define an almost rectangular frame (Fig. 3). In the direction perpendicular to this frame successive frames are mutually staggered in the direction orthogonal to the ligand planes, creating an undulating rectangular-sectioned framework that extends through the lattice.

Although the hydrogen atoms of the water molecules are not well resolved, there are several O_{water}–O_{resorcinol} distances less than 3 Å that are suggestive of hydrogen bonds in which the water molecule would act as the hydrogen donor (Table 3).

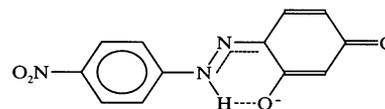
3.2. Spectra

The IR spectrum of the new complex shows a broad band at 3400–3500 cm⁻¹ due to water molecules. A

broad band at 3265 cm⁻¹ that is not present in the spectrum of the free ligand may be assigned to the ν (NH) vibration of the hydrazone tautomer. The hydrazone structure is also shown by the medium band at 1685 cm⁻¹ due to ν (C=O), which is likewise absent from the spectrum of the free ligand.

The complex is insoluble in water, and only moderately soluble in DMSO. In the latter solvent, it was nevertheless possible to record a ¹H NMR spectrum, although O–H and N–H signals were missing, presumably because of exchange with the water present as an impurity in DMSO. The resonances of the C–H protons of the complex lie slightly upfield of those of the free ligand.

The UV–Vis spectrum of the complex in water shows two strong peaks at 202 and 449 nm, near those of the free ligand, suggesting that in dilute aqueous solution the complex is largely dissociated. In acetone, however, the spectrum of the complex shows two different strong bands at 438 nm (close to the ligand band around 430 nm) and the other (which has no counter-



Scheme 2.

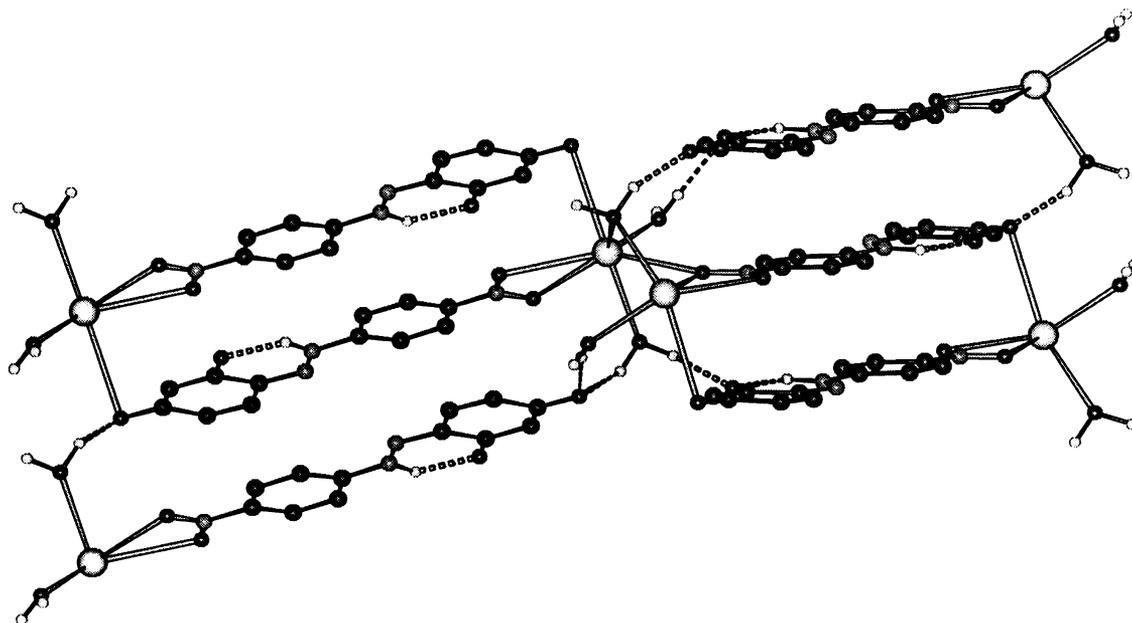


Fig. 3. Plot showing the rectangular $K-O_4-K^{ii}-O^{ii}$ frame (ii: $-x+1, -y+2, -z$) and the hydrogen bonding scheme.

Table 3
Intra- and intermolecular hydrogen bonding (Å, °) in $[K(HL)(OH_2)_2]_{\infty}$

D-H...A	$d(D-H)$ (Å)	$d(H...A)$ (Å)	$d(D...A)$ (Å)	$\angle(DHA)$ (°)
N2-HO2...O2	1.07	1.80	2.529(8)	121.2
O5-H51...O2 ⁱ	1.04	1.98	2.845(6)	137.9
O5-H52...O4 ⁱⁱ	1.00	1.88	2.759(7)	145.4
O6-H61...O2 ⁱⁱⁱ	0.86	2.05	2.917(8)	179.6
O6-H62...O4 ^{iv}	0.63	2.11	2.716(10)	162.8

Symmetry transformations: (i) $x, -y+5/2, z-1/2$; (ii) $-x+2, -y+2, -z$; (iii) $x-1, -y+5/2, z-1/2$; (iv) $x-1, -y+3/2, z-1/2$.

part in the spectrum of the ligand in this solvent) at 544 nm. The band of longer wavelength may be due to the hydrazone form and the other to the azo form (an hypothesis supported by the presence of a strong broad band centered at 514 nm in the diffuse reflectance spectrum of the complex). After 24 h the band at 544 nm disappears, indicating the disappearance of the hydrazone form (possibly due to slow dissociation).

3.3. Thermal analysis

Thermal analysis showed six weight losses between room temperature and 990 °C. In the first transition, a 9.053% weight loss between 40 and 200 °C corresponds basically to the loss of the two coordinated water molecules. The second, third and fourth transitions (200–500 °C) involve loss of NH_3 and together leave only material corresponding to KNO_3 . The fifth transition (500–650 °C) reduces KNO_3 to KNO_2 and the

sixth transition (650–900 °C) appears to convert KNO_2 into KO_2 .

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 158300 for compound $[K(HL)(OH_2)_2]_{\infty}$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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