Versatile Behaviour of the Cyclohexane-1,2-dione Bis(semicarbazone) Ligand in Mono- and Di-nuclear Metal Complexes†

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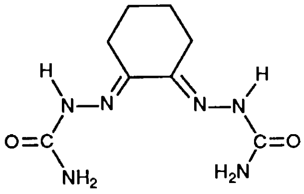
The chelating properties of cyclohexane-1,2-dione bis(semicarbazone) (H_2chds) were considered by means of IR spectroscopy and the crystal structures of $[Co_2(H_2chds)_2(OH_2)_3(NO_3)][NO_3]_3$ **1**, $[Ni(H_2chds)_2][NO_3]_2 \cdot 2H_2O$ **2** and $H_2chds \cdot H_2O$. The structure of **1** is triclinic, space group $P\bar{1}$, with a = 13.616(2), b = 12.694(2), c = 11.537(2) Å, α = 68.13(1), β = 63.37(1), γ = 70.01(1)°, Z = 2 and R = 0.0778. The crystals of **2** are also triclinic, space group $P\bar{1}$, a = 13.504(4), b = 13.221(5), c = 8.333(5) Å; α = 98.00(3), β = 77.71(4), γ = 106.43(3)°, Z = 2 and R = 0.0688. The $H_2chds \cdot H_2O$ molecule crystallizes in the space group $P2_1/c$ with a = 7.350(1), b = 15.469(3), c = 10.270(3) Å; β = 93.98(2)°, Z = 4 and R = 0.0372. The behaviour of the ligand is different in each structure: in **1** nearly planar tetradentate and accommodated in the equatorial positions of pentagonal bipyramids; in **2** distorted-octahedral co-ordination is provided by two tridentate ligand molecules having one urea group free. The free molecule is nearly planar with a different conformation: its arms are folded in such a way that an intramolecular N–H···O hydrogen bond is allowed. The structure of **1** is quite original: dimers are formed by means of two carbonylic bridges; the apices of the two polyhedra are occupied by two water molecules and a nitrate ion and one water molecule respectively.

Semicarbazones continue to occupy an important position as ligands in metal co-ordination chemistry. This general class of compounds exhibits a wide range of stereochemistries in complexation with transition-metal ions.[1-3] We are currently interested in the chelating properties of organic polydentate molecules containing the C(O)NH moiety, in order to isolate new metal complexes of different stereochemistries and nuclearity.[3-5] As part of this research programme we have prepared the bis(semicarbazone) H_2chds from the reaction of cyclohexane-1,2-dione and semicarbazide. In this paper we report the synthesis, the IR spectroscopic characterization and the X-ray structural analysis of $H_2chds \cdot H_2O$ and the metal complexes $[Co_2(H_2chds)_2(OH_2)_3(NO_3)][NO_3]_3$ and $[Ni(H_2chds)_2][NO_3]_2 \cdot 2H_2O$.

Experimental

All reactants were reagent grade. Cyclohexane-1,2-dione was purchased from Aldrich Chemical. Elemental C, H and N analyses were carried out on Perkin Elmer model 240 automatic equipment. The metals were determined by atomic absorption spectroscopy using a Perkin Elmer 303-HGA 70 instrument. Infrared spectra were recorded in the range 4000–200 cm^{-1} using a Nicolet 5PC FT-IR spectrophotometer, electronic spectra (200–900 nm) using a Kontron UVIKON 860 spectrophotometer.



H_2chds

*Preparations.—Cyclohexane-*1,2-*dione bis*(*semicarbazone*). To cyclohexane-1,2-dione (0.6 g, 0.005 mol), dissolved in methanol (50 cm^3) an aqueous solution (20 cm^3) of semicarbazide (1.2 g, 0.011 mol) in its neutral form (molar ratio 1:2) was added. A small amount of a pale yellow product was immediately formed; the suspension was then refluxed for about 2 h. The final pale yellow microcrystalline product was filtered off and washed with small portions of water (yield 50%; m.p. 240 °C). IR: ν(NH) 3426ms, 3350m, 3270m, 3210ms, ν(CO) amide I 1696s, 1677s, ν(CN) 1584ms, amide II 1494m, amide III 1322m cm^{-1}.

$[Co_2(H_2chds)_2(OH_2)_3(NO_3)][NO_3]_3$ **1**. To a methanol solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.12 g, 4.4 × 10^{-4} mol) was added solid H_2chds (0.1 g) under a nitrogen atmosphere. The red-orange solution was refluxed for about 2 h and then allowed to stand at room temperature (r.t.). After some days brown crystals were isolated (yield *ca.* 35%) (Found: C, 22.70; H, 3.85; Co, 13.40; N, 25.35. Calc. for $C_{16}H_{34}Co_2N_{16}O_{19}$: C, 22.05; H, 3.95; Co, 13.50; N, 25.70%).

$[Ni(H_2chds)_2][NO_3]_2 \cdot 2H_2O$ **2**. To a methanol solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.06 g, 2.2 × 10^{-4} mol) was added H_2chds (0.1 g) and the resulting green solution was refluxed for about 2 h. After slow evaporation of the solvent at r.t. green-brown crystals were isolated (yield *ca.* 50%) (Found: C, 29.35; H, 4.70; N, 28.70; Ni, 8.15. Calc. for $C_{16}H_{32}N_{14}NiO_{12}$: C, 28.60; H, 4.80; N, 29.20; Ni, 8.75%).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

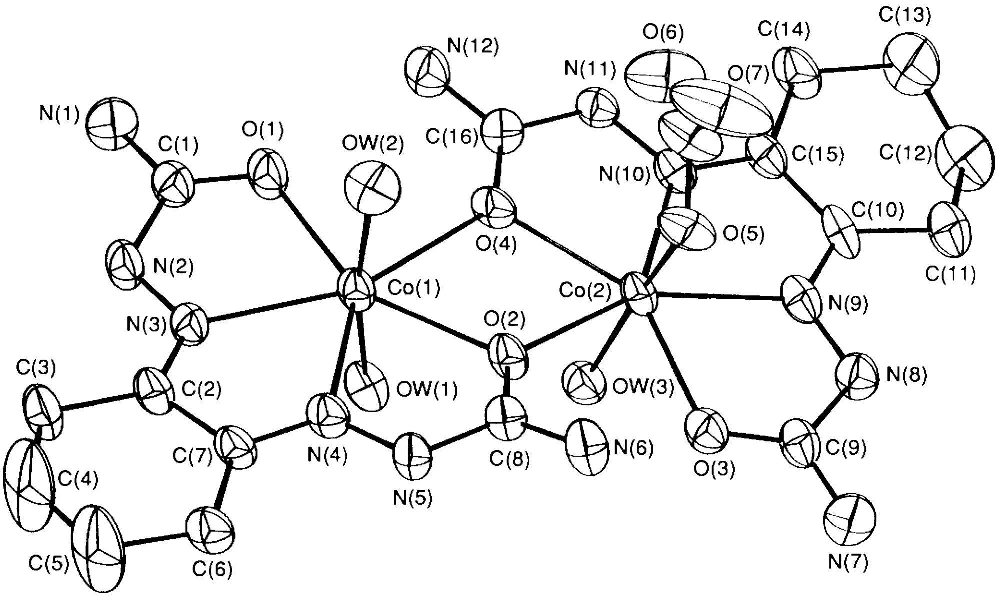


Fig. 1 Perspective view of the $[Co(H_2chds)_2(OH_2)_3(NO_3)]^{3+}$ cation

Crystallography.—Intensity data for all the compounds were collected by mounting the crystals on the diffractometers in a random orientation; the resulting crystal data with details of the data collection and refinements are in Table 1. The structures of complexes **1** and **2** were solved by Patterson and Fourier methods, while that of the ligand by direct methods. Refinements were carried out by full-matrix least squares using anisotropic thermal parameters for non-hydrogen atoms; hydrogens were introduced in the last refinement cycle. Some of these in **1** were placed at calculated positions and not refined; those of OW(1) were not located. In **1** and **2** the cyclohexane rings show some disorder allowing in some cases the location of two distinct peaks of electron density and population parameters are reported in the Tables of the coordinates. In addition in **1** the oxygen atoms of a nitrate ion are located over two different sites with population parameters 0.75 and 0.25. In **2** the two water molecules are statistically distributed over two sites with occupancy factors 0.68 and 0.32 for OW(1), 0.64 and 0.36 for OW(2). The final atomic coordinates for non-hydrogen atoms are in Tables 2–4. All the calculations were carried out on a Gould 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. di Parma using SHELX,[6] SHELX 86,[7] ORTEP[8] and PARST[9] programs.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Discussion

This is our first structural investigation on the chelating properties of a bis(semicarbazone) derived from an aliphatic diketone. Although we report the synthesis and structure of only two metal complexes with cyclohexane-1,2-dione bis(semicarbazone), the versatility of this organic molecule is well evidenced by comparing the cobalt and nickel complexes as far as the stoichiometry, the ter- and tetra-dentate ligand behaviour, and the mono- and di-nuclear nature are concerned.

A comparison of the main vibrational bands in the IR spectra of the cobalt and nickel complexes with those observed for the unco-ordinated H_2chds leads to the following considerations. In the 4000–3000 cm^{-1} region four bands are observed in the spectra of all three compounds, the more intense absorptions falling at *ca.* 3400 and 3200 cm^{-1}; all the bands undergo a negative shift ($\Delta\nu$ 10–30 cm^{-1}) upon co-ordination. An almost similar spectroscopic pattern is observed in the spectra of the two metal complexes, in agreement with their hydrated nature and the presence of the neutral form of the semicarbazone ligand. The spectra of both complexes exhibit a strong absorption at 3184 cm^{-1} due to the nitrate group. As regards the ν(CO) bands it is of note that for the cobalt complex a more marked splitting of the bands (1690s and 1650s cm^{-1}) is observed with respect to that of the nickel complex (1710w and 1675s cm^{-1}), where one co-ordinated and one unco-ordinated CO group is present. The electronic spectra, in methanol solution, show absorptions in the ultraviolet region (complex **1**, 308; **2**, 295 and 368 nm) which are attributable to π–π^* transitions of the chromophore system. The poor solubility of both complexes in most common solvents prevented the recording of absorption maxima in the 400–900 nm region.

The structure of complex **1** (Fig. 1) is quite unexpected since the same reaction with $Ni(NO_3)_2\cdot6H_2O$ affords a complex differing in ligand:metal ratio and in co-ordination geometry. Two tetradentate ligand molecules (N,N′,O,O′) are each bonded to a metal centre occupying the equatorial plane of a pentagonal bipyramid: the fifth site is provided by the O(2) and O(4) carbonylic oxygens which are bridging two cobalt atoms so that the polyhedra share an edge. The apical sites are occupied by two water molecules for Co(1), the O(5) nitrate oxygen and a water molecule for Co(2), thus the two polyhedra are not equivalent. Each polyhedron contains four five-membered chelate rings in which the ligand fragment is planar and the metal deviates by 0.236(1), −0.049(1), −0.271(1) Å [rings with O(1) and N(3), N(3) and N(4), N(4) and O(2), respectively] and −0.245(1), −0.081(1), −0.073(1) Å [rings with O(3) and N(9), N(9) and N(10), N(10) and O(4), respectively]. The donor atoms in the pentagonal planes are in different arrangements in the two polyhedra: around Co(1) these show significant discrepancies from planarity [maximum deviation 0.134(8) Å]; those related to Co(2) are roughly planar [maximum deviation 0.035(9) Å]. The metal deviates from these mean planes by 0.040(1) Å for Co(1) and −0.155(1) Å for Co(2); the dihedral angle between the planes O(2)Co(1)O(4) and O(2)Co(2)O(4) is 11.1(2)°. The axial angles 170.4(3) and 170.3(3)° are indicative of a moderate distortion and the short OW(1) ··· OW(3) 2.879(7) Å distance probably corresponds to a hydrogen bond. The ligand molecules, on the whole, show significant displacements from planarity, but considering the dihedral angles formed between the planar fragments [OCCN ∧ NCCN, molecule 1, range 9.5(3)–15.8(3)°; molecule 2, range 1.8(4)–4.4(5)°] the molecule around Co(2) is closer to

Table 1 Experimental data for the crystallographic analyses

Compound	**1**	**2**	$H_2chds{\cdot}H_2O$
Formula	$C_{16}H_{34}Co_2N_{16}O_{19}$	$C_{16}H_{32}N_{14}NiO_{12}$	$C_8H_{16}N_6O_3$
M	872.40	671.25	244.25
Crystal symmetry	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	13.616(2)	13.504(4)	7.350(1)
b/Å	12.694(2)	13.221(5)	15.469(3)
c/Å	11.537(2)	8.333(5)	10.270(3)
α/°	68.13(1)	98.00(3)	90
β/°	63.37(1)	77.71(4)	93.98(2)
γ/°	70.01(1)	106.43(3)	90
U/Å^3	1617.1(5)	1389(1)	1164.8(4)
Z	2	2	4
D_c/g cm^{-3}	1.792	1.604	1.393
D_m/g cm^{-3}	1.83	1.65	1.43
Reflections for lattice parameters (number, θ range/°)	11, 10.3–14.4	21, 22–38	25, 9.4–16.9
F(000)	896	700	520
T/K	294	294	294
Diffractometer	Siemens AED	Siemens AED	CAD4
Crystal size/mm	0.29 × 0.54 × 0.65	0.28 × 0.37 × 0.28	0.16 × 0.29 × 0.65
μ/cm^{-1}	11.25	17.23	1.02
Scan speed/° min^{-1}	2.5–12	3.5–12	0.69–3.3
Scan width/°	1.3 + 0.35 tan θ	1.3 + 0.35 tan θ	1.3 + 0.35 tan θ
Radiation, λ/Å	0.710 79	1.5418	0.710 79
θ range/°	3–25	3–70	3–25
h,k,l range	−18 to 18, −17 to 17, 0–16	−16 to 16, −16 to 16, 0–10	−8 to 8, −18 to 18, 0–12
Standard reflection	−3 7 1	9 1 2	1 7 3
Maximum intensity variation(%)	3.1	3.2	4.0
Scan mode	ω–2θ	ω–2θ	ω–2θ
No. of measured reflections	6036	5675	2254
No. of reflections used in the refinement [$I > 3\sigma(I)$]	3436	4609	1001
No. of reflections suppressed in the final refinements	11	32	16
No. of refined parameters	475	480	194
$R = \Sigma\vert\Delta F\vert/\Sigma\vert F_o\vert$	0.0778	0.0688	0.0372
$R' = [\Sigma w(\Delta F^2)/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0795	0.0809	0.0411
k,g in $w = k/[\sigma^2(F_o) + gF_o^2]$	1.0, 9.67 × 10^{-3}	1.0, 3.9 × 10^{-4}	1.0, 4.12 × 10^{-3}
Maximum, minimum height in final Δ*F*/e Å^{-3}	−0.72, 0.43	−1.8, 0.92	−0.72, 0.43

Table 2 Fractional atomic coordinates for complex **1** (× 10^5 for Co × 10^4 for others) with estimated standard deviations (e.s.d.s) in parentheses. The atoms A have population parameter 0.75 and atoms B 0.25

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Co(1)	26 192(9)	12 673(9)	32 701(11)	N(5)	4 993(5)	1 230(5)	1 161(7)
Co(2)	21 967(9)	43 643(9)	14 007(11)	N(6)	5 171(6)	3 108(6)	209(8)
OW(1)	1 959(5)	1 271(5)	1 936(6)	N(7)	4 304(6)	5 921(7)	−2 436(8)
OW(2)	3 207(5)	1 569(6)	4 495(6)	N(8)	2 580(6)	6 513(6)	−934(7)
OW(3)	1 478(5)	3 686(5)	558(6)	N(9)	1 779(6)	6 161(6)	266(7)
O(1)	1 254(5)	720(5)	5 072(6)	N(10)	537(5)	5 215(6)	2 474(7)
O(2)	3 465(4)	2 663(4)	1 611(6)	N(11)	−58(5)	4 576(6)	3 674(7)
O(3)	3 480(5)	4 651(5)	−549(6)	N(12)	−127(6)	2 819(6)	5 170(8)
O(4)	1 413(4)	3 068(5)	3 272(6)	N(13)	2 805(6)	5 155(8)	3 102(9)
O(5)	3 165(5)	4 884(6)	2 024(6)	N(14)	8 541(7)	3 947(6)	2 563(8)
O(6)	1 841(6)	5 126(8)	3 877(8)	N(15)	2 217(7)	8 643(6)	1 519(9)
O(7)	3 451(7)	5 464(10)	3 334(11)	N(16)	3 732(8)	9 027(8)	−3 198(10)
O(8A)	7 849(9)	3 548(9)	3 596(9)	C(1)	1 212(7)	−315(7)	5 534(9)
O(9A)	8 368(9)	4 985(8)	2 011(9)	C(2)	3 890(7)	−1 276(7)	3 444(9)
O(10A)	9 420(8)	3 256(8)	2 075(9)	C(3)	4 200(8)	−2 556(7)	3 915(10)
O(8B)	7 616(56)	4 643(59)	3 008(66)	C(4)	5 416(13)	−3 008(11)	3 249(21)
O(9B)	9 018(35)	4 608(35)	1 479(39)	C(5)	6 071(11)	−2 475(10)	2 116(19)
O(10B)	9 042(52)	3 098(52)	2 838(60)	C(6)	5 854(7)	−1 203(7)	1 618(9)
O(11)	2 510(7)	7 738(7)	1 204(12)	C(7)	4 715(7)	−618(7)	2 338(9)
O(12)	1 327(7)	8 865(8)	2 375(9)	C(8)	4 516(6)	2 378(7)	993(8)
O(13)	2 842(6)	9 343(6)	923(7)	C(9)	3 483(7)	5 637(7)	−1 289(9)
O(14)	4 581(8)	8 204(8)	−3 438(11)	C(10)	855(7)	6 848(7)	731(9)
O(15)	3 878(7)	9 994(6)	−3 477(9)	C(11)	504(8)	8 072(7)	30(10)
O(16)	2 855(8)	8 786(9)	−2 762(13)	C(12)	−725(11)	8 541(10)	661(13)
N(1)	368(6)	−745(7)	6 552(8)	C(13)	−1 202(10)	8 208(10)	2 101(12)
N(2)	2 094(6)	−1 113(6)	4 956(8)	C(14)	−1 017(7)	6 928(7)	2 733(10)
N(3)	2 948(6)	−638(5)	3 924(7)	C(15)	121(7)	6 283(7)	2 038(9)
N(4)	4 346(6)	488(6)	2 109(7)	C(16)	447(6)	3 435(7)	4 037(8)

Table 3 Fractional atomic coordinates for complex **2** (× 10^5 for Ni, × 10^4 for others) with e.s.d.s in parentheses. The population parameters are: OW(1A) 0.68, OW(1B) 0.32, OW(2A) 0.64, OW(2B) 0.36, C(4A) 0.70, C(4B) 0.30, C(12A) 0.60 and C(12B) 0.40

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni	37 695(6)	29 879(6)	35 926(11)	N(14)	975(5)	7 457(5)	5 737(1)
O(1)	4 941(2)	4 029(2)	2 032(4)	C(1)	4 947(4)	4 971(4)	2 428(7)
O(2)	729(3)	1 412(3)	5 141(6)	C(2)	2 821(4)	4 477(4)	5 740(7)
O(3)	4 997(2)	2 750(2)	4 607(4)	C(3)	2 540(5)	5 477(5)	6 481(9)
O(4)	2 952(3)	4 474(4)	1 342(6)	C(4A)	1 428(19)	5 286(19)	7 416(31)
O(5)	6 044(4)	−1 874(4)	1 612(7)	C(4B)	1 960(41)	5 401(41)	8 060(68)
O(6)	6 346(4)	−469(4)	3 291(7)	C(5)	1 139(1)	4 413(8)	8 473(1)
O(7)	5 201(4)	−703(4)	1 709(7)	C(6)	1 285(6)	3 374(6)	7 696(9)
O(8)	509(5)	7 762(5)	7 100(9)	C(7)	2 235(4)	3 439(4)	6 377(7)
O(9)	571(6)	6 575(6)	5 069(1)	C(8)	1 283(4)	1 043(4)	5 768(8)
O(10)	1 816(5)	8 020(6)	5 048(1)	C(9)	5 206(4)	1 884(4)	4 070(7)
N(1)	5 602(2)	5 770(5)	1 643(9)	C(10)	3 089(4)	913(4)	1 996(7)
N(2)	4 265(4)	5 244(4)	3 810(6)	C(11)	2 959(6)	−242(5)	1 505(1)
N(3)	3 587(3)	4 406(3)	4 543(5)	C(12A)	1 801(18)	−830(17)	1 298(29)
N(4)	2 636(3)	2 665(3)	5 732(6)	C(12B)	2 201(20)	−734(20)	314(34)
N(5)	2 170(4)	1 671(4)	6 315(6)	C(13)	1 412(9)	−255(8)	388(2)
N(6)	1 102(5)	15(5)	5 975(9)	C(14)	1 378(5)	841(5)	1 026(9)
N(7)	6 004(5)	1 601(6)	4 410(1)	C(15)	2 321(4)	1 456(4)	1 760(7)
N(8)	4 602(4)	1 180(4)	3 093(6)	C(16)	2 073(4)	4 026(5)	2 028(8)
N(9)	3 818(3)	1 511(3)	2 725(6)	OW(1A)	−2 964(9)	3 134(9)	7 034(14)
N(10)	2 537(3)	2 458(4)	2 184(6)	OW(2A)	−3 895(10)	2 640(10)	−3(17)
N(11)	1 772(4)	2 965(4)	2 152(7)	OW(1B)	1 899(18)	6 674(17)	1 731(27)
N(12)	1 314(5)	4 526(5)	2 672(9)	OW(2B)	−3 314(19)	2 991(20)	8 817(32)
N(13)	5 857(4)	−1 022(4)	2 211(7)				

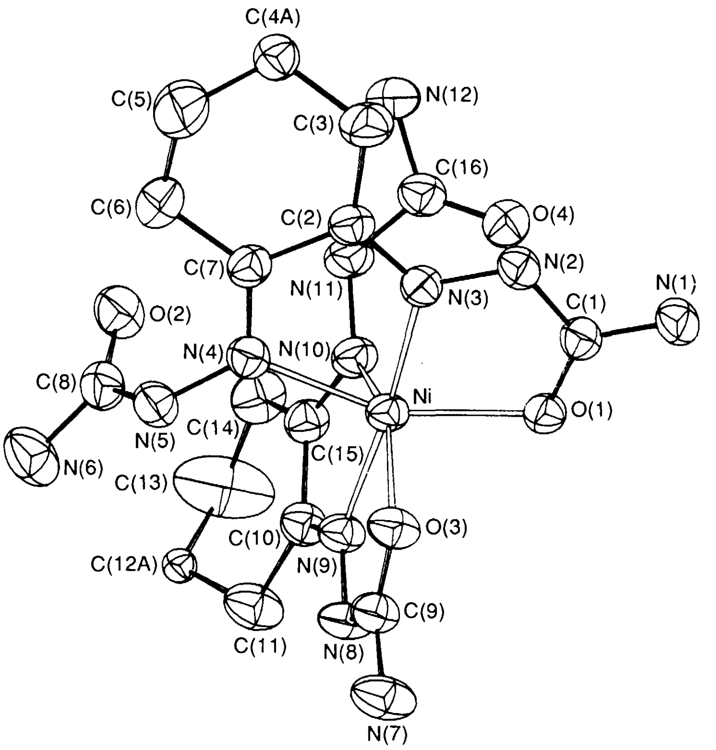


Fig. 2 Perspective view of the $[Ni(H_2chds)_2]^{2+}$ cation

planarity than is the other. Pentagonal-bipyramidal geometry is not common in cobalt(II) complexes and few crystal structures of such compounds are present in the literature.[10–22] As far as we know, this seems to be the first dinuclear cobalt(II) complex with bipyramidal geometry. Bond distances involving the metal atoms (Table 5) can be considered as belonging to three groups: (*a*) equatorial non-bridging; (*b*) equatorial bridging; (*c*) axial. The first group agree well with those of the literature which fall in the range 2.15–2.21 Å, the second are longer [the bridges are asymmetrical and the pairs related to each oxygen are significantly different only for O(4) ($\Delta/\sigma = 11.3$)] and the Co(1)–OW distances are identical and shorter than the equatorial values, while those of Co(2) are both longer and different from each other [the nitrate oxygen is more strictly co-ordinated than the OW(3) atom]. The equatorial values are close to the ideal value of 72° calculated for a pentagonal base; the values in O(1)–Co(1)–O(4) 82.5(2)° and O(2)–Co(2)–O(3) 79.2(2)° are justified as involving oxygens of both ligands not constrained in a chelated ring. The angles formed with the axial oxygens reveal that the Co(1) polyhedron is more regular [82.9(2)–98.9(3)°] than that of Co(2) [82.3(2)–101.0(2)°]. The packing of the molecules

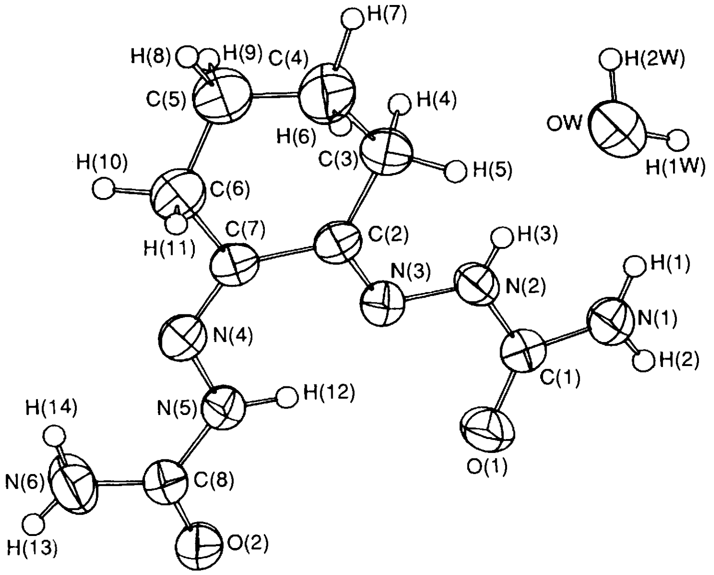


Fig. 3 An ORTEP view of the molecule $H_2chds \cdot H_2O$

Table 4 Fractional atomic coordinates (× 10^4) for the ligand

Atom	*X/a*	*Y/b*	*Z/c*
O(1)	6441(4)	7129(1)	−208(2)
O(2)	5824(4)	5641(1)	−3679(2)
OW	8125(5)	6254(2)	4212(3)
N(1)	6368(4)	7511(2)	1907(3)
N(2)	7203(4)	6149(2)	1383(3)
N(3)	7316(4)	5511(2)	480(2)
N(4)	7426(4)	4139(2)	−1366(2)
N(5)	6867(4)	4916(2)	−1888(3)
N(6)	6521(6)	4233(2)	−3868(4)
C(1)	6643(4)	6952(2)	947(3)
C(2)	7858(4)	4750(2)	873(3)
C(3)	8392(5)	4555(2)	2278(3)
C(4)	9196(9)	3660(2)	2537(4)
C(5)	8424(8)	2993(3)	1692(4)
C(6)	8477(6)	3170(2)	272(4)
C(7)	7878(4)	4072(2)	−135(3)
C(8)	6355(4)	4956(2)	−3181(3)
H(1)	6618(41)	7366(20)	2713(34)
H(2)	6140(35)	8013(20)	1695(25)
H(3)	7485(58)	6049(25)	2117(41)
H(4)	9377(55)	5031(32)	2632(43)
H(5)	7191(55)	4599(22)	2823(32)
H(6)	9035(69)	3485(24)	3541(44)
H(7)	10630(68)	3699(32)	2375(43)
H(8)	9147(58)	2398(25)	1915(34)
H(9)	7014(58)	2921(23)	1905(35)
H(10)	9866(56)	3084(32)	17(44)
H(11)	7607(36)	2707(22)	−255(34)
H(12)	6821(49)	5356(23)	−1306(34)
H(13)	6156(54)	4204(26)	−4644(39)
H(14)	6866(56)	3773(26)	−3450(40)
H(1W)	8014(68)	5848(34)	4928(55)
H(2W)	7765(62)	6837(39)	4513(50)

involves a large system of hydrogen bonding involving all nitrate oxygens, water molecules and the majority of the NH groups.

The $[Ni(H_2chds)_2]^{2+}$ cation is shown in Fig. 2, and bond distances and angles involving the nickel atom are reported in Table 6. The metal is surrounded by two ligand molecules acting in a tridentate manner (O,N,N′) with one urea group free. Each ligand produces two roughly planar five-membered chelate rings with nickel deviating from these planes by −0.022(2), 0.328(2), 0.154(2) and −0.287(1) Å [for O(1)C(1)N(2)N(3), N(3)C(2)C(7)N(4), O(3)C(9)N(8)N(9) and N(9)C(10)C(15)N(10) respectively]. The co-ordination can be described as very distorted octahedral. The distortion is particularly evident from the angles at the metal: those of the chelated rings are more similar to those of a pentagonal base with values ranging from 75.8(2) to 77.1(2)°. The *trans* angles are significantly different: those involving the atoms of the terminal portions of chelated rings are 152.3(2) and 152.6(2)° while the N(3)–Ni–N(9) angle is 174.9(2)°; all these values are justified by the steric constraints exerted by the ligands upon chelation. The Ni–O bond distances 2.116(3) and 2.128(4) Å are similar while Ni–N show significant differences, the shortest involving the N(3) and N(9) 'central' atoms [1.992(4) and 2.000(5) Å] which seems to be the best site for co-ordination. The remaining values [2.093(4) and 2.141(5) Å] are considerably longer, but all these distances are in agreement with values found for octahedral nickel complexes, *e.g.* μ-3,6-dichloro-2,5-dihydroxy-1,4-benzoquininato-bis[(2,2′,2″-triaminotriethylamine)nickel(II)] tetraphenylborate[23] [Ni–O 2.129(4), 2.044(4); Ni–N 2.085(5), 2.110(4), 2.142(4) Å] and (μ-oxalato-*O,O′,O″,O‴*)bis(3,7,11-trimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene-*N,N′,N″*)dinickel(II)diperchlorate[24] [Ni–O 2.125(4) and 2.069(4); Ni–N 2.200(3), 2.187(3), 2.157(4) and 1.990(3) Å]. The urea groups are planar; those unco-ordinated are tilted with respect to the chelated rings, the torsion angles around the N–N bonds being C(7)N(4)N(5)C(8) 80.1(7)° and C(15)N(10)N(11)C(16) 22.2(5°), while the corresponding values in the chelated rings are 7.2(5) and 9.1(5)° for N(2)–N(3) and N(8)–N(9) bonds respectively. The packing involves all these groups with nitrate ions in a network of hydrogen bonds.

The behaviour of the ligand is different in each of the three structures: in **1** it is nearly planar tetradentate, in **2** non-planar tridentate, in the free molecule is approximately planar with a conformation different from that in **1**. The arms of the molecule are folded (Fig.3) in such a way that the intramolecular hydrogen bond N(5)–H(12)··· N(3) 137(3)°, N(5)··· N(3) 2.600(3) Å, H(12)··· N(3) 1.86(3) Å is allowed. All NH groups, oxygen atoms and the water molecule are involved in the hydrogen-bond system. The fragment N(3)C(2)C(7)N(4)N(5)-C(8)N(6)O(2) is almost planar and the C(1)N(1)N(2)O(1) group is planar: these form a dihedral angle of 11.5(2)° and accordingly the O(1)C(1)N(2)N(3) torsion angle is −7.9(5)°. The non-coplanarity of these fragments could be explained as

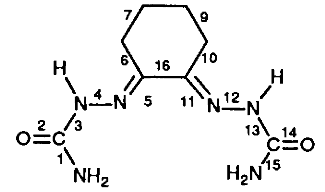
Table 5 Bond distances (Å) and angles (°) in the co-ordination polyhedron for complex **1**

Co(1)–OW(1)	2.099(9)	Co(2)–OW(3)	2.167(9)
Co(1)–OW(2)	2.099(10)	Co(2)–O(2)	2.268(5)
Co(1)–O(1)	2.145(5)	Co(2)–O(3)	2.132(5)
Co(1)–O(2)	2.241(5)	Co(2)–O(4)	2.235(5)
Co(1)–O(4)	2.315(5)	Co(2)–O(5)	2.119(9)
Co(1)–N(3)	2.196(6)	Co(2)–N(9)	2.190(6)
Co(1)–N(4)	2.208(6)	Co(2)–N(10)	2.151(6)
N(3)–Co(1)–N(4)	68.3(3)	O(3)–Co(2)–O(4)	147.0(2)
O(4)–Co(1)–N(4)	139.5(2)	O(2)–Co(2)–N(10)	141.5(2)
O(4)–Co(1)–N(3)	151.5(3)	O(2)–Co(2)–N(9)	149.4(3)
O(2)–Co(1)–N(4)	70.3(2)	O(2)–Co(2)–O(5)	82.5(3)
O(2)–Co(1)–N(3)	138.2(2)	O(2)–Co(2)–O(4)	70.2(2)
O(2)–Co(1)–O(4)	69.2(2)	O(2)–Co(2)–O(3)	79.2(2)
O(1)–Co(1)–N(4)	137.8(3)	OW(3)–Co(2)–N(10)	89.6(3)
O(1)–Co(1)–N(3)	70.6(2)	OW(3)–Co(2)–N(9)	93.8(3)
O(1)–Co(1)–O(4)	82.5(2)	OW(3)–Co(2)–O(5)	170.3(3)
O(1)–Co(1)–O(2)	151.3(2)	OW(3)–Co(2)–O(4)	82.3(2)
OW(2)–Co(1)–N(4)	90.7(3)	OW(3)–Co(2)–O(3)	85.8(2)
OW(2)–Co(1)–N(3)	98.9(3)	OW(3)–Co(2)–O(2)	90.1(2)
OW(2)–Co(1)–O(4)	88.4(2)	Co(1)–O(1)–C(1)	120.0(6)
OW(2)–Co(1)–O(2)	87.2(2)	Co(1)–O(2)–Co(2)	110.3(2)
OW(2)–Co(1)–O(1)	86.8(3)	Co(2)–O(2)–C(8)	132.8(5)
OW(1)–Co(1)–N(4)	93.3(3)	Co(1)–O(2)–C(8)	117.0(5)
OW(1)–Co(1)–N(3)	90.7(3)	Co(2)–O(3)–C(9)	119.7(6)
OW(1)–Co(1)–O(4)	82.9(2)	Co(1)–O(4)–Co(2)	108.8(2)
OW(1)–Co(1)–O(2)	85.9(2)	Co(2)–O(4)–C(16)	116.5(5)
OW(1)–Co(1)–O(1)	96.1(3)	Co(1)–O(4)–C(16)	134.6(5)
OW(1)–Co(1)–OW(2)	170.4(3)	Co(2)–O(5)–N(13)	124.3(7)
N(9)–Co(2)–N(10)	68.9(3)	Co(1)–N(3)–N(2)	116.1(5)
O(5)–Co(2)–N(10)	100.1(3)	Co(1)–N(3)–C(2)	123.3(6)
O(5)–Co(2)–N(9)	89.4(3)	Co(1)–N(4)–C(7)	121.8(6)
O(4)–Co(2)–N(10)	71.6(2)	Co(1)–N(4)–N(5)	116.4(5)
O(4)–Co(2)–N(9)	140.4(3)	Co(2)–N(9)–N(8)	115.9(5)
O(4)–Co(2)–O(5)	101.0(2)	Co(2)–N(9)–C(10)	122.1(6)
O(3)–Co(2)–N(10)	139.1(3)	Co(2)–N(10)–C(15)	122.6(6)
O(3)–Co(2)–N(9)	70.8(2)	Co(2)–N(10)–N(11)	117.1(5)
O(3)–Co(2)–O(5)	86.7(3)		

Table 6 Bond distances (Å) and angles (°) in the co-ordination polyhedron for complex **2**

Ni–O(3)	2.128(4)	Ni–N(4)	2.093(4)
Ni–O(1)	2.116(3)	Ni–N(9)	2.000(5)
Ni–N(3)	1.992(4)	Ni–N(10)	2.141(5)
N(9)–Ni–N(10)	75.8(2)	O(3)–Ni–N(3)	106.2(2)
N(4)–Ni–N(10)	88.7(2)	O(3)–Ni–O(1)	87.5(2)
N(4)–Ni–N(9)	99.6(2)	Ni–O(3)–C(9)	112.4(4)
N(3)–Ni–N(10)	101.3(2)	Ni–O(1)–C(1)	112.6(3)
N(3)–Ni–N(9)	174.9(2)	Ni–N(3)–N(2)	116.1(4)
N(3)–Ni–N(4)	76.0(2)	Ni–N(3)–C(2)	119.8(4)
O(1)–Ni–N(10)	102.1(2)	Ni–N(4)–C(7)	114.8(4)
O(1)–Ni–N(9)	107.5(2)	Ni–N(4)–N(5)	125.6(4)
O(1)–Ni–N(4)	152.6(2)	Ni–N(9)–C(10)	120.1(4)
O(1)–Ni–N(3)	77.1(2)	Ni–N(9)–N(8)	115.7(4)
O(3)–Ni–N(10)	152.3(2)	Ni–N(10)–C(15)	113.4(4)
O(3)–Ni–N(9)	76.6(2)	Ni–N(10)–N(11)	126.5(4)
O(3)–Ni–N(4)	94.6(2)		

Table 7 Comparative bond distances (Å) and angles (°) in the ligand molecule



	1	**2**	H_2chds·H_2O
(1)	1.319(10), 1.313(9)	1.331(11), 1.321(8)	1.338(4)
(2)	1.224(9), 1.231(10)	1.256(7), 1.242(6)	1.216(4)
(3)	1.366(10), 1.368(9)	1.387(7), 1.355(7)	1.375(4)
(4)	1.355(9), 1.351(8)	1.347(6), 1.357(8)	1.360(4)
(5)	1.262(9), 1.274(9)	1.289(7), 1.282(7)	1.299(4)
(6)	1.482(10), 1.483(11)	1.493(9), 1.495(8)	1.501(4)
(7)	1.482(17), 1.495(14)	1.51(2), 1.57(2) 1.38(5), 1.51(2)	1.518(5)
(8)	1.293(21), 1.434(18)	1.46(2), 1.41(3) 1.48(4), 1.37(3)	1.439(6)
(9)	1.469(15), 1.496(13)	1.49(1), 1.48(1)	1.487(5)
(10)	1.471(10), 1.491(11)	1.493(9), 1.504(9)	1.514(4)
(11)	1.287(10), 1.278(9)	1.288(8), 1.289(7)	1.289(4)
(12)	1.339(9), 1.355(8)	1.395(6), 1.388(8)	1.366(4)
(13)	1.357(9), 1.368(9)	1.377(7), 1.358(8)	1.357(4)
(14)	1.269(8), 1.254(8)	1.231(9), 1.222(6)	1.229(4)
(15)	1.299(11), 1.292(9)	1.340(9), 1.351(9)	1.333(5)
(16)	1.466(11), 1.456(10)	1.483(7), 1.476(9)	1.474(4)
(1,2)	125.7(8), 124.2(8)	124.1(6), 123.4(6)	123.9(3)
(1,3)	116.4(8), 115.3(8)	113.6(6), 115.6(5)	113.7(3)
(2,3)	119.4(8), 119.0(8)	120.2(5), 120.1(6)	122.3(3)
(3,4)	113.4(7), 113.2(7)	114.9(5), 115.6(5)	117.7(3)
(4,5)	120.4(7), 121.9(7)	123.9(5), 124.0(5)	118.5(3)
(5,6)	126.3(9), 125.6(9)	125.6(5), 125.0(6)	122.5(3)
(6,7)	112(1), 112.4(9)	113(1), 112(1)	115.2(3)
(7,8)	125(1), 116(1)	117(1), 113(2)	114.4(4)
(8,9)	122(1), 115(1)	114.5(7), 118(1)	115.1(3)
(9,10)	114(1), 113.3(9)	114.5(7), 113.5(8)	114.4(3)
(10,11)	125.1(8), 125.4(8)	126.1(6), 124.5(5)	113.3(3)
(11,12)	121.7(8), 120.3(7)	118.6(5), 116.6(5)	120.3(3)
(12,13)	116.9(7), 115.9(7)	119.4(5), 118.2(5)	118.6(3)
(13,14)	117.8(8), 118.8(8)	121.9(7), 122.0(6)	120.4(3)
(13,15)	117.5(8), 116.0(8)	113.6(6), 114.4(6)	116.8(3)
(14,15)	124.7(8), 125.2(8)	124.5(6), 123.6(5)	122.8(3)
(5,16)	113.2(7), 112.4(8)	112.7(5), 113.6(5)	116.4(2)
(11,16)	113.3(8), 113.8(8)	114.5(5), 115.5(5)	128.1(2)

consequence of a better orientation for the hydrogen bonds which the N(2)–H(3) and N(1)–H(1) groups form with the water molecule: OW deviates from this last plane by only 0.534(5) Å. Comparative bond distances and angles of the ligand molecules are in Table 7: there is general agreement of the values; differences involve only C=O [1.216(4)–1.269(8) Å, Δ/σ = 5.9] and N–N bonds [1.339(9)–1.395(6) Å, Δ/σ = 5.2] while the differences in the cyclohexane ring are scarcely significant in view of high thermal parameters and disorder concerning these atoms. Similar considerations can be applied to the bond angles, relevant differences in the free ligand are found for C(6)–C(7)–N(4) 113.3(3)° and C(2)–C(7)–N(4) 128.1(2)°, which could be justified as a consequence of the intramolecular hydrogen bond. The molecules are connected in the crystal by the following hydrogen bonds: OW ··· O(1$^{\text{I}}$) 2.870(4), H(2W) ··· O(1$^{\text{I}}$) 1.90(5) Å, OW–H(2W) ··· O(1$^{\text{I}}$) 163(4)°; N(1) ··· O(1$^{\text{I}}$) 3.012(4), H(1) ··· O(1$^{\text{I}}$) 2.29(3) Å, N(1)–H(1) ··· O(1$^{\text{I}}$) 141(3)°; N(1) ··· O(2$^{\text{I}}$) 2.942(4), H(2) ··· O(2$^{\text{I}}$) 2.13(3) Å, N(1)– H(2) ··· O(2$^{\text{I}}$) 173(2)°; N(6) ··· O(2$^{\text{II}}$) 2.958(4), H(13) ··· O(2$^{\text{II}}$) 2.19(4) Å, N(6)–H(13) ··· O(2$^{\text{II}}$) 155(4)°; OW ··· O(2$^{\text{III}}$) 2.992(4), H(1W) ··· O(2$^{\text{III}}$) 2.25(5) Å, OW–H(1W) ··· O(2$^{\text{III}}$) 132(4)° (I $x,\frac{3}{2} - y,z - \frac{1}{2}$; II $1 - x,1 - y,-1 - z$; III $x,y,z + 1$) and by several van der Waals contacts which are responsible for the packing.

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