Ni(II) and Zn(II) complexes with cinoxacin. Synthesis and characterization of $M(Cx)_2(DMSO)_n(H_2O)_m$ ($n=0$, 2; $m=2$, 4). Crystal structures of $[M(Cx)_2(DMSO)_2]\cdot 4H_2O$ (M = Ni(II), Zn(II))

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Abstract

New metal complexes of cinoxacin (HCx = 1-ethyl-1,4-dihydro-4-oxo(1,3)dioxolo(4,5-g)cinnoline-3-carboxylic acid) were synthesized, isolated as $[Zn(Cx)_2(DMSO)_2]\cdot 4H_2O$, $[Ni(Cx)_2(DMSO)_2]\cdot 4H_2O$, $Zn(Cx)_2\cdot 4H_2O$ and $Ni(Cx)_2\cdot 2H_2O$, and characterized by elemental analysis, TG studies, IR and UV–Vis spectroscopic techniques. The crystal and molecular structures of the complexes $[M(Cx)_2(DMSO)_2]\cdot 4H_2O$ (M = Zn(II), Ni(II)) have been determined by X-ray structure analysis. The crystals of $[Zn(Cx)_2(DMSO)_2]\cdot 4H_2O$ are triclinic, space group $P\bar{1}$ with unit cell dimensions $a=8.950(4)$, $b=9.168(5)$, $c=11.650(6)$ Å, $\alpha=69.06(1)$, $\beta=82.05(1)$, $\gamma=75.63(1)°$, $V=863.6(8)$ Å^3; $[Ni(Cx)_2(DMSO)_2]\cdot 4H_2O$ is monoclinic, space group $P2_1/n$, $a=10.684(2)$, $b=7.729(1)$, $c=20.862(1)$ Å, $\beta=104.66(1)°$, $V=1666.7(3)$ Å^3. Both structures consist of monomeric $[M(Cx)_2(DMSO)_2]$ units, and uncoordinated water molecules that provide crystalline stability through a network of hydrogen bond interactions. The metal ion is placed in a crystallographic inversion centre, which relates to the two bidentate cinoxacinate ligands that bind through one carboxylate oxygen atom and the exocyclic carbonyl oxygen atom. The octahedral coordination environment is completed by two dimethyl sulfoxide molecules coordinated via the oxygen atom. The characterization of the $Ni(Cx)_2\cdot 2H_2O$ complex suggests an octahedral arrangement to the Ni(II) ion.

Introduction

The antibacterial activity of 4-quinolone compounds, such as nalidixic acid (HNal), oxolinic acid or cinoxacin (HCx = 1-ethyl-1,4-dihydro-4-oxo(1,3)dioxolo(4,5-g)cinnoline-3-carboxylic acid) (Fig. 1), is apparently due to the inhibition of DNA synthesis. It has been shown that these drugs are specific inhibitors of the DNA-gyrase, the enzyme responsible for converting double-stranded DNA into a negative superhelical form. Actually, it seems that chelation of certain metal ions through the carbonyl and carboxyl groups of these molecules and the binding of the resulting complex to DNA (with some base specificity), may be essential prerequisites for their antibacterial activity [1].

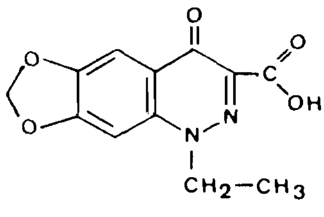

Fig. 1. Cinoxacin (HCx = 1-ethyl-1,4-dihydro-4-oxo(1,3)dioxolo-(4,5-g)cinnoline-3-carboxylic acid).

Solid-state IR and ESR studies of $M(Nal)_n$ complexes [2] suggest that they are formed by interaction through the carboxylate group with no apparent interaction of the keto group. However, studies carried out in solution on the coordination chemistry of nalidixic acid with metal ions suggest that in those conditions the coordination mode is via the 4-oxo and 3-carboxylate groups, although no definitive evidence has been shown [3, 4]. A recent ^{13}C NMR study [5] indicates that the nalidixate ion exhibits the ability to act as a chelate ligand towards Cu(II) ions in aqueous solution and that the site of

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binding depends upon the nature of the other co-ligands present in solution. In the absence of those added co-ligands, chelation via the 3-carboxylate group is observed, while interaction when 1,10-phenanthroline is present is produced through the 3-carboxylate and 4-oxo groups.

We have initiated studies on the coordination chemistry of HCx with transition and d^{10} metal ions in an attempt to examine its mode of binding in the solid state. We first reported the synthesis and thermal behaviour of several complexes of HCx with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) [6, 7]. The synthesis and crystal structure of the complex $[Co(Cx)_3]Na \cdot 6H_2O$ has also been reported; this structure consists of anionic monomeric units of $[Co(Cx)_3]^-$ and sodium cations. Three cinoxacinate ions are chelating through the O_{ceto} and O_{carbox} atoms with the Co(II) ion bonded to six oxygen atoms in a slightly distorted octahedral environment [8].

In order to enhance the information on the coordination properties of this drug, we report here the synthesis and characterization of new metal complexes of cinoxacin and the crystal structures of the complexes $[M(Cx)_2(DMSO)_2] \cdot 4H_2O$ (M = Ni(II), Zn(II)).

Experimental

Cinoxacin was supplied by Lilly Indiana Laboratories as a powder material. All reagents used are of analytical grade.

Synthesis of $[Zn(Cx)_2(DMSO)_2] \cdot 4H_2O$ *(I)*

The compound was obtained in DMSO medium, by mixing solutions containing 0.1 mmol (0.03 g) of cinoxacin and 0.1 mmol (0.02 g) of $ZnCl_2$. To the resulting solution, 1 ml of a 0.1 M aqueous solution of NaOH was added with stirring. The final volume was 100 ml. After 12–14 days, a white precipitate, **III**, was obtained. It was filtered, washed with water and dried at 90 °C. The remaining solution was allowed to stand at room temperature and crystals of compound **I**, suitable for an X-ray structural determination, appeared after a few days. These crystals were separated by filtration and dried at room temperature. Approx. yield for **I**: 6%; for **III**: 75%. *Anal.* for compound **I**: Calc. for $C_{28}H_{38}N_4O_{16}S_2Zn$: C, 41.2; H, 4.7; N, 6.9; S, 7.9; Zn, 8.0. Found: C, 41.0; H, 5.0; N, 6.5; S, 7.8; Zn, 8.2%. Compound **III** ($Zn(Cx)_2 \cdot 4H_2O$): Calc. for $C_{24}H_{26}N_4O_{14}Zn$: C, 43.7; H, 3.9; N, 8.5; Zn, 9.9. Found: C, 43.1; H, 3.7; N, 8.4; Zn, 10.1%.

Synthesis of $[Ni(Cx)_2(DMSO)_2] \cdot 4H_2O$ *(II)*

The complex was prepared as follows. DMSO solutions of cinoxacin (HCx) (0.5 mmol; 0.13 g) and $NiSO_4 \cdot 7H_2O$ (0.17 mmol; 0.05 g) were mixed. Then, 5 ml of 0.1 M NaOH was added slowly with continuous stirring. The final volume was 100 ml. After standing for 1 day, a large amount of microcrystalline green compound, **IV**, appeared, which was filtered, washed with water and dried at 90 °C. From the remaining solution, a few green crystals of compound **II** were formed within a period of two to three months. Crystals were collected by filtration and dried at room temperature. All attempts to obtain crystals of compound **IV** suitable for an X-ray investigation failed. Approx. yield for **II**: 10%; for **IV**: 80%. *Anal.* for compound **II**: Calc. for $C_{28}H_{38}N_4O_{16}S_2Ni$: C, 41.5; H, 4.7; N, 6.9; S, 7.9; Ni, 7.3. Found: C, 41.0; H, 4.8; N, 7.0; S, 7.1; Ni, 7.1%. Compound **IV** ($Ni(Cx)_2 \cdot 2H_2O$): Calc. for $C_{24}H_{22}N_4O_{12}Ni$: C, 46.7; H, 3.6; N, 9.1; Ni, 9.5. Found: C, 46.4; H, 3.2; N, 8.9; Ni, 9.3%.

Analyses

The content of Ni and Zn was determined by atomic absorption spectroscopy with a model 2380 Perkin-Elmer spectrometer. C, H, N and S analyses were obtained with an elemental analyzer, model MGO 1106 Carlo Erba.

Physical measurements

IR absorption spectra were obtained with a Perkin-Elmer spectrophotometer, model 843. Samples were prepared as KBr discs for the range 4000–600 cm^{-1} and CsI discs for the range 600–200 cm^{-1}. The UV–Vis–near-IR absorption spectra were recorded with

TABLE 1. Summary of crystal data and collection of intensities of the compounds $[Zn(Cx)_2(DMSO)_2] \cdot 4H_2O$ (**I**) and $[Ni(Cx)_2(DMSO)_2] \cdot 4H_2O$ (**II**)

	I	**II**
Empirical formula	$C_{28}H_{38}N_4O_{16}S_2Zn$	$C_{28}H_{38}N_4O_{16}S_2Ni$
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	8.950(4)	10.684(2)
b (Å)	9.168(5)	7.729(1)
c (Å)	11.650(6)	20.862(1)
α (°)	69.06(1)	90.00
β (°)	82.05(1)	104.66(1)
γ (°)	75.63(1)	90.00
V (Å^3)	863.6(8)	1666.7(3)
Z	1	2
Formula weight	816.1	809.47
Calc. density (g cm^{-3})	1.569	1.613
μ (cm^{-1})	9.180	7.815
$F(000)$	424	844
Independent reflections	6194	3690
Observed reflections	3466 ($I > 3\sigma(I)$)	2500 ($I > 3\sigma(I)$)
Final R	0.041	0.038
Final R_w	0.043	0.041
Final s	1.07	1.22

a Perkin-Elmer model Lambda 9 spectrophotometer, by use of the diffuse-reflectance technique with MgO as a reference. Thermogravimetric analyses were made in air and nitrogen atmospheres using Perkin-Elmer 3600 and DTA 1700 instruments at a heating rate of 10 °C min^{-1}.

Structure determination

Information concerning conditions for crystallographic data collection and structure refinement is summarized in Table 1 for both compounds.

Compound I

A crystalline piece, $0.27 \times 0.23 \times 0.23$ mm size, was cut from a large crystal and mounted at room temperature in a Siemens R3m/v diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å). 25 centred reflections were used for determining the orientation matrix and unit cell. Reflections were collected by the ω-scan technique. Four standard reflections measured every 90 min showed no significant changes. Data were corrected for Lp but not for absorption.

The metal atom was placed in a symmetry centre (only possibility for $P\bar{1}$ and $Z = 1$), the other non-H atoms found in a ΔF map and refined anisotropically. All hydrogen atoms located were clearly seen in subsequent ΔF maps, those of cinoxacin and DMSO were introduced in ideal positions with free rotation for methyl groups, and water hydrogens were refined with fixed O–H distances. The function minimized was $\Sigma w(\Delta F)^2$ with $w^{-1} = \sigma^2(F) + 0.0015F^2$. Largest Δ/σ in the final cycle, 0.001 for non-H atoms; largest difference peak and hole in the final ΔF map, 0.32 and -0.42 e Å^{-3}. All calculations and drawings were made on a MicroVAXII computer with the SHELXTL PLUS program package [9]. Scattering factors were included in this software. Final atomic coordinates are listed in Table 2.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for $[\text{Zn(Cx)}_2(\text{DMSO})_2] \cdot 4\text{H}_2\text{O}$

Atom	*x*	*y*	*z*	U_{eq}[a]
Zn	5000	5000	5000	31(1)
N(1)	2257(2)	6884(2)	8965(2)	31(1)
C(11)	1305(3)	7949(3)	9621(2)	41(1)
C(12)	−300(4)	7646(4)	9973(3)	61(2)
N(2)	2306(2)	7560(2)	7754(2)	31(1)
C(2)	3057(3)	6750(3)	7038(2)	28(1)
C(1)	2989(3)	7765(3)	5673(2)	28(1)
O(1)	3804(2)	7221(2)	4889(2)	38(1)
O(2)	2111(2)	9112(2)	5415(2)	47(1)
C(3)	3854(3)	5097(3)	7523(2)	27(1)
O(3)	4590(2)	4266(2)	6881(1)	36(1)
C(4)	3754(3)	4382(3)	8845(2)	26(1)
C(5)	4499(3)	2762(3)	9419(2)	31(1)
C(6)	4389(3)	2180(3)	10666(2)	32(1)
O(4)	5016(3)	694(2)	11435(2)	47(1)
C(7)	4527(4)	691(3)	12665(2)	47(1)
O(5)	3694(3)	2265(2)	12585(2)	47(1)
C(8)	3589(3)	3129(3)	11370(2)	34(1)
C(9)	2869(3)	4682(3)	10870(2)	33(1)
C(10)	2946(3)	5319(3)	9566(2)	28(1)
S(1)	7408(1)	7201(1)	4860(1)	38(1)
O(6)	7167(2)	5506(2)	5202(2)	45(1)
C(21)	8027(4)	7758(4)	3272(3)	56(1)
C(22)	9190(3)	6958(3)	5485(3)	47(1)
O(1W)	815(3)	10105(3)	3135(2)	57(1)
O(2W)	1875(3)	7286(4)	2465(3)	83(1)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Compound II

A parallelepipedic bright green single crystal ($0.30 \times 0.30 \times 0.25$ mm) was mounted on an Enraf-Nonius CAD-4 diffractometer. The unit cell was determined and refined from angle data of 25 randomly selected reflections in the range $8 < \theta < 14°$. Intensities were measured at room temperature with filtered Mo Kα radiation by the ω/θ scan technique. 3690 reflections were collected in the range $3 < \theta < 26°$ corresponding to 3308 unique ($R_{int} = 0.027$) of which 2500 with $I > 3\sigma(I)$ were used in structure determination and refinement. Lorentz–polarization and empirical absorption [10] corrections were applied (absorption: min. 0.795, max.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}_2 \times 10^3$) for $[\text{Ni(Cx)}_2(\text{DMSO})_2] \cdot 4\text{H}_2\text{O}$

Atom	*x*	*y*	*z*	U_{eq}
Ni	5000	0000	5000	24.0(2)
N(1)	−232(2)	−1220(4)	4016(1)	28(1)
C(11)	−1555(3)	−1239(5)	3560(2)	38(2)
C(12)	−1624(4)	−416(7)	2909(2)	58(3)
N(2)	678(2)	−467(3)	3789(1)	28(1)
C(2)	1887(3)	−441(4)	4144(1)	25(1)
C(1)	2783(3)	508(4)	3800(1)	25(1)
O(1)	3920(2)	847(3)	4127(1)	27.5(9)
O(2)	2334(2)	884(3)	3207(1)	37(1)
C(3)	2299(3)	−1243(4)	4786(1)	23(1)
O(3)	3451(2)	−1301(3)	5133(1)	29(1)
C(4)	1278(3)	−2034(4)	5024(1)	25(1)
C(5)	1572(3)	−2799(4)	5663(2)	32(1)
C(6)	561(3)	−3467(4)	5867(2)	32(1)
O(4)	583(2)	−4272(4)	6454(1)	47(1)
C(7)	−744(3)	−4476(6)	6467(2)	49(2)
O(5)	−1508(2)	−4153(4)	5805(1)	47(1)
C(8)	−702(3)	−3411(4)	5474(2)	33(1)
C(9)	−1037(3)	−2707(5)	4860(2)	34(2)
C(10)	1(3)	−1991(4)	4630(1)	26(1)
S(1)	5477(1)	2998(1)	6049(1)	34.3(4)
O(6)	4434(2)	2166(3)	5501(1)	35(1)
C(21)	5429(5)	5200(6)	5891(2)	63(2)
C(22)	4844(5)	3039(7)	6753(2)	74(3)
O(1W)	3604(3)	2617(4)	2406(1)	63(1)
O(2W)	9902(3)	6313(5)	1705(1)	64(1)

1.133). The structure was solved by direct methods [11] and refined by full-matrix least-squares with unit weights and anisotropic thermal parameters for non-H atoms. All H atoms were located from a difference Fourier map and included in the structure factor calculation with $B_{iso}=4.0$ Å^2, but not refined. The secondary-extinction coefficient [12] was refined to $g=4.734\times10^{-7}$ $\{F_o=F_c/[1+g(F_c)^2\mathrm{Lp}]\}$. $\Delta/\sigma_{max}<0.001$, $\Delta\rho$ max. 0.344 e Å^{-3}. Final R factor 0.038, R_w 0.041, S 1.223 for 233 parameters. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [13]. Calculations were performed on a DEC MicroVAXII computer with the SDP program package [14]. Final positional parameters are given in Table 3.

Results and discussion

Structural studies

Both structures consist of monomeric [M(Cx)$_2$(DMSO)$_2$] units, and uncoordinated water molecules that provide crystalline stability through a network of hydrogen bond interactions. The metal atom placed in a crystallographic inversion centre relates the two bidentate cinoxacinate ligands that bind through one oxygen of the carboxylate group and the exocyclic carbonyl oxygen. The octahedral coordination environment is completed by two dimethyl sulfoxide molecules coordinated via their oxygen atom (Figs. 2 and 3).

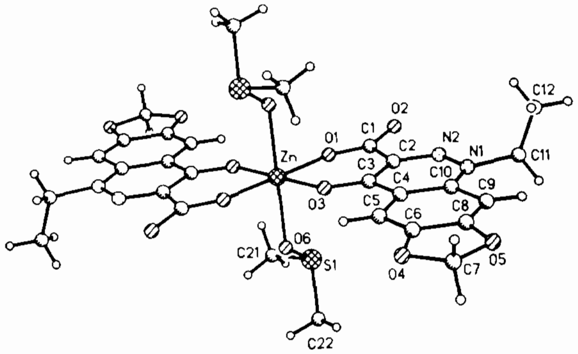

Fig. 2. View of the molecule of [Zn(Cx)$_2$(DMSO)$_2$].

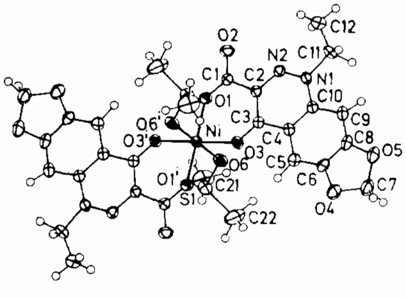

Fig. 3. ORTEP drawing of [Ni(Cx)$_2$(DMSO)$_2$].

The distortion of the octahedron is not severe (see distances and angles in Table 4), with the distances metal–O(DMSO) slightly longer than the other M–O distances. These last bond lengths are similar to those observed in related compounds [8, 15]. The geometry of coordinated solvent molecules is similar to that observed in other DMSO complexes of zinc [16] and nickel [17].

Distances and angles within the cinoxacinate ion are similar to those described for the free cinoxacin [18] with the expected changes in the carboxylate group area due to its deprotonation, as already reported for the [Co(Cx)$_3$]$^-$ anion [8]. The three rings of the ligand are almost coplanar with dihedral angle values lower than 5°; the maximum deviations from planarity in a single ring are found in the O-containing ring.

In the [Zn(Cx)$_2$(DMSO)$_2$]·4H$_2$O complex, the C(12)–C(11)–N(1)–N(2) torsion angle is 97.6°; in the parent ligand, 97.0(2)°. This indicates that in both compounds the plane defined by the ethyl group atoms is almost perpendicular to the cinoxacin ring system. However, in the [Ni(Cx)$_2$(DMSO)$_2$]·4H$_2$O complex this angle is 1.0(5)° showing that, as a result of the complexation, there is a rotation along the N(1)–C(11) bond with C(11) lying on the molecular plane. It should be noted that in the previously reported Co(II)–Cx complex the mentioned angle is 82.7°.

Intermolecular hydrogen bonds with symmetry codes are given in Tables 5 and 6. A stereoscopic view of the compounds is shown in Figs. 4 (**I**) and 5 (**II**). Two interstitial water molecules complete the asymmetric unit in both complexes and are connected via a hydrogen bond with the O(2) and O(6) atoms (compound **I**) and with the two O-carboxylate atoms (compound **II**) contributing to stabilize the structure.

General physicochemical characteristics of the complexes

Due to the impossibility of obtaining structural information from single crystal X-ray diffraction of compounds **III** and **IV**, an attempt was made to clarify their nature by other physical measurements.

The Zn(II) complexes (**I** and **III**) are soluble in DMF and the Ni(II) complexes (**II** and **IV**) in DMF and DMSO. All isolated compounds are insoluble in MeOH and EtOH; in aqueous solutions they decompose with ligand precipitation.

The low value for molar conductivity in dimethylformamide of compound **III** ($\Lambda_{mol}=39.5\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$) suggests its partial dissociation. Moreover, the Λ_{mol} value in dimethyl sulfoxide for compound **IV** ($12.0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$) corresponds to a non-electrolyte behaviour [19].

Table 7 shows the values of λ_{max} from diffuse reflectance measurements and the IR absorption bands

TABLE 4. Bond lengths (Å) and angles (°) for $[Zn(Cx)_2(DMSO)_2]\cdot 4H_2O$ (**I**) and $[Ni(Cx)_2(DMSO)_2]\cdot 4H_2O$ (**II**), with e.s.d.s in parentheses

	I	II
M–O(1)	2.019(2)	2.003(2)
M–(O(3)	2.058(2)	2.015(2)
M–O(6)	2.164(3)	2.140(2)
N(1)–C(11)	1.484(4)	1.491(4)
N(1)–N(2)	1.322(3)	1.320(4)
N(1)–C(10)	1.375(3)	1.377(4)
C(11)–C(12)	1.505(5)	1.485(6)
N(2)–C(2)	1.319(3)	1.317(3)
C(2)–C(1)	1.529(3)	1.522(5)
C(2)–C(3)	1.445(3)	1.440(4)
C(1)–O(1)	1.256(3)	1.262(3)
C(1)–O(2)	1.246(3)	1.244(3)
C(3)–O(3)	1.263(3)	1.260(3)
C(3)–C(4)	1.442(3)	1.443(4)
C(4)–C(5)	1.421(3)	1.419(4)
C(4)–C(10)	1.417(4)	1.404(4)
C(5)–C(6)	1.355(3)	1.360(5)
C(6)–O(4)	1.365(3)	1.369(4)
C(6)–C(8)	1.408(4)	1.391(4)
O(4)–C(7)	1.439(4)	1.434(5)
C(7)–O(5)	1.427(4)	1.439(5)
O(5)–C(8)	1.355(3)	1.359(4)
C(8)–C(9)	1.356(3)	1.353(5)
C(9)–C(10)	1.418(3)	1.428(5)
S(1)–O(6)	1.523(2)	1.522(2)
S(1)–C(21)	1.781(3)	1.770(4)
S(1)–C(22)	1.775(4)	1.766(5)
O(1)–M–O(3)	89.4(1)	89.07(8)
O(1)–M–O(6)	93.0(1)	91.10(8)
O(3)–M–O(6)	89.9(1)	88.83(9)
C(11)–N(1)–N(2)	113.5(2)	116.1(2)
C(11)–N(1)–C(10)	122.7(2)	120.6(3)
N(2)–N(1)–C(10)	123.7(2)	123.3(2)
N(1)–C(11)–C(12)	112.2(3)	113.5(3)
N(1)–N(2)–C(2)	120.9(2)	120.8(2)
N(2)–C(2)–C(1)	112.3(2)	112.7(2)
N(2)–C(2)–C(3)	122.4(2)	122.9(3)
C(1)–C(2)–C(3)	125.3(2)	124.4(2)
C(2)–C(1)–O(1)	119.6(2)	118.7(2)
C(2)–C(1)–O(2)	116.5(2)	116.8(2)
O(1)–C(1)–O(2)	123.9(2)	124.5(4)
M–O(1)–C(1)	132.0(1)	132.7(2)
C(2)–C(3)–O(3)	125.1(2)	125.0(3)
C(2)–C(3)–C(4)	115.5(2)	115.0(2)
O(3)–C(3)–C(4)	119.5(2)	120.0(3)
M–O(3)–C(3)	127.6(1)	128.3(2)
C(3)–C(4)–C(5)	120.1(2)	119.5(2)
C(3)–C(4)–C(10)	119.5(2)	119.7(3)
C(5)–C(4)–C(10)	120.3(2)	120.7(3)
C(4)–C(5)–C(6)	117.0(2)	116.6(3)
C(5)–C(6)–O(4)	128.7(2)	128.2(3)
C(5)–C(6)–C(8)	122.0(2)	122.2(3)
O(4)–C(6)–C(8)	109.2(2)	109.7(3)
C(6)–O(4)–C(7)	106.2(2)	105.9(2)
O(4)–C(7)–O(5)	107.8(2)	106.6(3)
C(7)–O(5)–C(8)	106.7(2)	106.4(2)
C(6)–C(8)–O(5)	109.8(2)	109.4(3)
C(6)–C(8)–C(9)	123.4(2)	123.8(3)
O(5)–C(8)–C(9)	126.8(2)	126.9(3)
C(8)–C(9)–C(10)	115.8(2)	115.6(3)
N(1)–C(10)–C(4)	118.0(2)	118.4(3)
N(1)–C(10)–C(9)	120.6(2)	120.6(2)
C(4)–C(10)–C(9)	121.4(2)	121.1(3)
O(6)–S(1)–C(21)	105.1(2)	107.1(2)
O(6)–S(1)–C(22)	104.6(1)	105.7(2)
C(21)–S(1)–C(22)	98.7(2)	97.9(2)
M–O(6)–S(1)	122.8(1)	117.0(1)

TABLE 5. Probable hydrogen bonds for $[Zn(Cx)_2(DMSO)_2\cdot 4H_2O$ (**I**)

A–H...B	A–B (Å)
O(1W)–H(11W)–O(2)	2.798(3)
O(1W)–H(12W)–O(2^{i})	2.989(3)
O(2W)–H(21W)–O(1W)	2.866(5)
O(2W)–H(22W)–O(6^{ii})	3.042(3)

Symmetry codes: $^{i}-x,\ 2-y,\ 1-z$; $^{ii}1-x,\ 1-y,\ 1-z$.

TABLE 6. Probable hydrogen bonds for $[Ni(Cx)_2(DMSO)_2]\cdot 4H_2O$ (**II**)

A–H...B	A–H (Å)	H...B (Å)	A–B (Å)	AHB (°)
O(1W)–H(11W)–O(2^{ii})	0.928(3)	2.011(2)	2.892(4)	157.9(2)
O(1W)–H(12W)–O(2)	0.995(3)	1.767(3)	2.753(4)	170.7(2)
O(2W)–H(21W)–O(1W^{iii})	0.948(3)	1.845(3)	2.784(4)	170.6(2)
O(2W)–H(22W)–O(1^{iii})	1.127(3)	1.939(2)	2.989(4)	153.4(2)

Symmetry codes: $^{ii}\frac{1}{2}-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$; $^{iii}\frac{3}{2}-x,\ \frac{1}{2}+x,\ \frac{1}{2}-z$.

in the region 4000–200 cm^{-1}. The IR spectra of the complexes exhibit a broad absorption between 3600 and 3000 cm^{-1} showing well defined maxima around 3440 cm^{-1}; these bands can be assigned to the O–H stretching vibrations of water molecules [20]. The band at 2600 cm^{-1}, due to hydrogen-bonded –COOH groups in cinoxacin, is absent in the complexes, thus confirming the complete deprotonation of the ligand. Furthermore, the IR spectra of the compounds present a broad band between 1660 and 1600 cm^{-1} which is slightly split and includes the vibrations ν_a(OCO) and ν(CO) (at 1735 and 1620 cm^{-1} in the ligand), justifying that interaction of these groups with the metallic ion exists; a fact which was confirmed by X-ray structure determination [2]. The IR spectra of compounds **I** and **II**, which contain coordinated DMSO, exhibit a new band at 1010 and 1000 cm^{-1}, respectively, that can be assigned to the $\nu(S{=}O)_{DMSO}$ vibration. This band is shifted to lower frequency when compared with the ν(S=O) band of

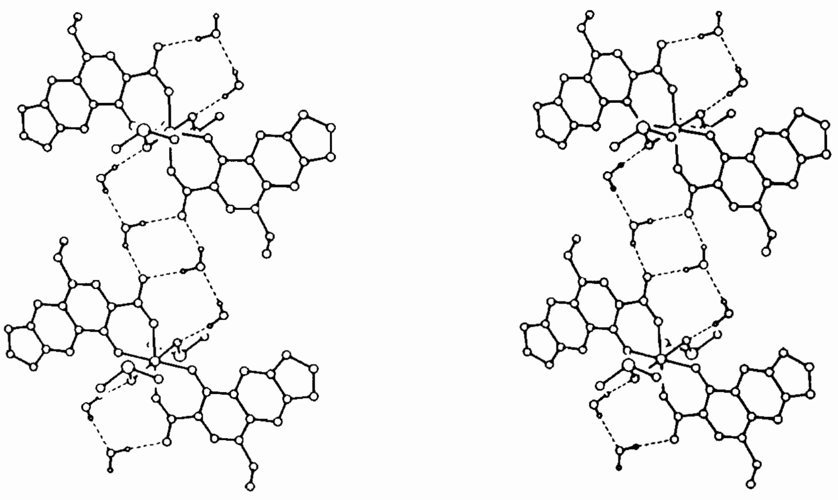

Fig. 4. Stereoscopic view of $[Zn(Cx)_2(DMSO)_2]\cdot 4H_2O$.

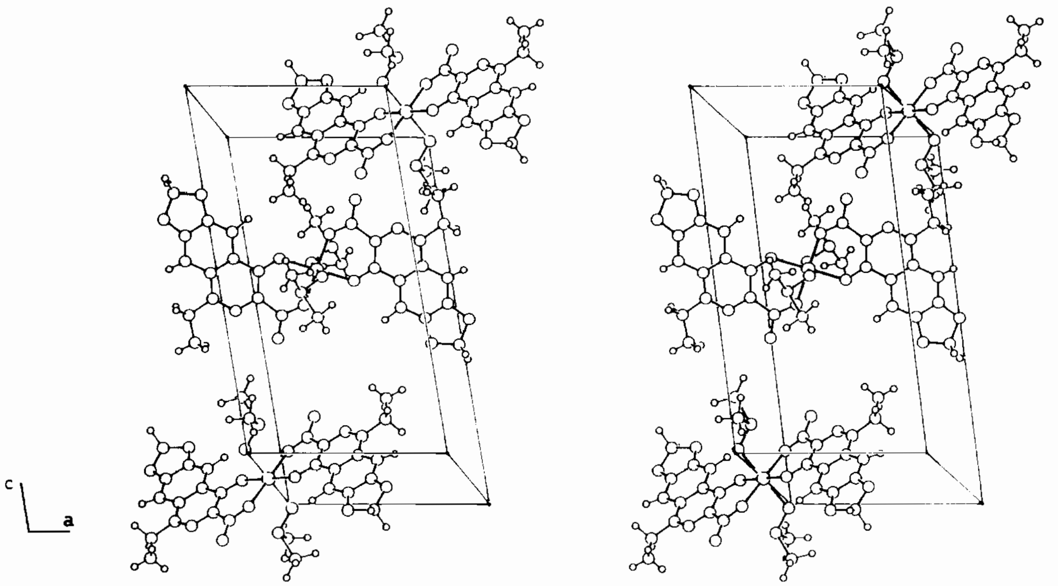

Fig. 5. Stereoscopic view of the cell of $[Ni(Cx)_2(DMSO)_2]\cdot 4H_2O$. (Water molecules have been omitted for illustrative purposes.)

TABLE 7. UV–Vis and IR bands

Compound	UV–Vis (cm^{-1})	IR (cm^{-1})
Cinoxacin		2600, 1735, 1620
I		3440, 1620, 1610, 1010, 530
II	25381, 14493, 8621, 25900	3400, 1660, 1640, 1600, 1000, 525
III		3440, 1620, 530
IV	26483, 15408, 8850, 25900	3440, 1660, 1640, 530

the DMSO free molecule, indicating that the solvent coordinates the metal in both compounds through the oxygen atom [21]. On the other hand, the IR spectra of all the complexes show a new band at 530 cm^{-1}, which is attributed to the ν(M–O) vibration [22].

The diffuse reflectance spectra of the Ni(II) compounds show d–d bands in the regions 7000–1300, 11 000–20 000 and 19 000–27 000 cm^{-1} and an MLCT band at about 2590 cm^{-1}. The d–d bands are assigned to the ν_1, ν_2 and ν_3 electronic transitions of an Ni(II) ion in an octahedral environment, in agreement with the crystal structure of compound **II**.

TG studies on the compounds $Zn(Cx)_2\cdot 4H_2O$ (**III**) and $Ni(Cx)_2\cdot 2H_2O$ (**IV**) show that water molecules are present in both cases. Theoretical weight loss percentages (10.91 and 5.83, respectively) for the dehydration process are in good agreement with experimental values (11.0 and 5.6, respectively). The endothermic effects associated with the elimination of these water molecules have been observed in DTA curves at different temperature ranges. The complex **III** exhibits endothermic effects at 90 and 125 °C attributable to loss of hydration water. The existence of two different types of water molecules can be explained either by the formation of different H bonds in the initial lattice or by the consecutive structural changes that can take place during the heating process. Complex **IV** presents only an endothermic change at 200 °C; this high temperature peak value suggests that the two water molecules are directly coordinated to Ni(II).

On the basis of all these measurements of compounds **III** and **IV**, the only conclusions which can be drawn are the following.

The IR data indicate a bidentate behaviour of the cinoxacinate ligand for all the compounds isolated. In these complexes the cinoxacinate anion binds through the O_{ceto} and O_{carbox} atoms. Thermogravimetric results for the compound $Zn(Cx)_2 \cdot 4H_2O$ (**III**) support the hypothesis that the four water molecules are not directly bonded to the metal ion. On account of this fact it is reasonable to propose that the metal environment in this compound is different from that observed in compound **I**.

From diffuse reflectance measurements and TG studies, we propose for the $Ni(Cx)_2 \cdot 2H_2O$ (**IV**) complex an octahedral geometry around the metal with two water molecules coordinating the Ni(II) ion. This behaviour is analogous to that described for the $[Ni(Cx)_2(DMSO)_2] \cdot 4H_2O$ compound.

Supplementary material

Anisotropic temperature factors, hydrogen atom coordinates and list of observed and calculated structure factors are available from the authors on request.

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