Inorganica Chimica Acta, *217* (1994) 149–154

Synthesis and characterization of Cd(II) complexes of cinoxacin. Crystal structure of a dicadmium complex containing two monoatomic-bridging carboxylate oxygen atoms

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(Received August 27, 1993; revised November 8, 1993)

Abstract

The reaction of $CdCl_2 \cdot 2\frac{1}{2}H_2O$ with cinoxacin in DMSO solution affords the $[Cd_2(Cx)_4(DMSO)_2] \cdot 2H_2O$ dimeric complex (**I**) which has been characterized by single crystal X-ray diffraction; complex **II** ($Cd(Cx)_2 \cdot H_2O$) was prepared by dissolving **I** in a minimum amount of water. Compound **I** is triclinic, space group $P\bar{1}$ with unit cell dimensions: $a = 8.960(1)$, $b = 12.084(5)$, $c = 13.696(6)$ Å, $\alpha = 73.96(4)$, $\beta = 84.69(4)$, $\gamma = 80.93(49)°$, $V = 1405.5(9)$ Å^3. Each dimer contains cadmium atoms bridged by two carboxylate oxygen atoms from two cinoxacinate (Cx) ligands generating planar Cd_2O_2 rings. The metal environment is formed by two O_{carbox} and O_{ceto} atoms from the cinoxacinate monoanions, one oxygen atom of the DMSO molecule and a carboxylate oxygen atom which acts as a bridge. One of the coordinated cinoxacinate molecules acts as a bidentate chelate and bridging ligand and the other one as a bidentate chelate ligand. The solid-state IR and ^{13}C NMR spectra of both compounds are discussed in detail with regard to the crystal structure of complex **I**.

Key words: Crystal structures; Cadmium complexes; Cinoxacin complexes; Dinuclear complexes

Introduction

Cinoxacin (HCx = 1-ethyl-1,4-dihydro-4-oxo(1,3)dioxolo(4,5-*g*)cinnoline-3-carboxylic acid) is a 4-quinolone derivative related to nalidixic (HNal) and oxolinic acids. These compounds are antibacterial agents employed as specific inhibitors of the bacterial DNA-gyrase, provided with different binding sites towards metal ions for the formation of metal complexes. So, solid-state IR and ESR studies of $M(Nal)_n$ complexes [1] suggest that they are formed by interaction through the carboxylate group with no apparent interaction of the keto group.

In the past few years we have been investigating the coordination chemistry of cinoxacin with transition and d^{10} metal ions in an attempt to examine its mode of binding in the solid [2–5]. The synthesis and crystal structure of the complex $[Co(Cx)_3]Na \cdot 6H_2O$ has already been reported [4]. More recently we have described the structure and chemical behavior of the cinoxacinate anion in the complexes $[M(Cx)_2(DMSO)_2] \cdot 4H_2O$ (M = Ni(II), Zn(II)) [5]. In all the compounds the cinoxacinate ions act as bidentate chelate ligands through one carboxylate oxygen atom and the exocyclic carbonyl oxygen atom. The metal ion is bonded to six oxygen atoms in a slightly distorted octahedral environment.

In the present paper we report the synthesis and spectroscopic characterization of two Cd(II) complexes with cinoxacin. We also report the crystal structure of the binuclear $[Cd_2(Cx)_4(DMSO)_2] \cdot 2H_2O$ compound. The complex described here is the first reported compound in which cinoxacin acts as bridging ligand via one of the oxygen atoms of the carboxylate group.

Experimental

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

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SSDI 0020-1693(93)03767-5

Synthesis of $[Cd_2(Cx)_4(DMSO)_2]\cdot 2H_2O$ (I)

The complex was prepared as follows. DMSO solutions of cinoxacin (0.11 g, 0.4 mmol) and $CdCl_2\cdot 2\frac{1}{2}H_2O$ (0.02 g, 0.1 mmol) were mixed. Then, 4 ml of NaOH 0.1 M was added slowly with continuous stirring. The final volume was 100 ml. By slow evaporation of the solution at room temperature white crystals of **I** suitable for X-ray structure determination were formed after a period of 2–3 months. Complex **II** was prepared by dissolving **I** in a minimum amount of water; the solution was allowed to stand at room temperature and crystals of compound **II** appeared after a few days. Approx. yield for **I**: 12%; for **II**: 80%. *Anal.* for compound **I**: Calc. for $C_{52}H_{52}N_8O_{24}S_2Cd_2$: C, 42.74; H, 3.56; N, 7.67; S, 4.39; Cd, 15.38. Found: C, 42.80; H, 3.51; N, 7.52; S, 4.30; Cd, 15.42%. Compound **II** ($Cd(Cx)_2\cdot H_2O$): Calc. for $C_{24}H_{20}N_4O_{11}Cd$: C, 44.11; H, 3.06; N, 8.57; Cd, 17.22. Found: C, 43.40; H, 3.08; N, 8.37; Cd, 17.00%.

TABLE 1. Crystal data and intensity collection parameters

Compound	$[Cd_2(Cx)_4(DMSO)_2]$ $2H_2O$
Formula	$Cd_2C_{52}H_{52}N_8O_{24}S_2$
Formula weight (g mol^{-1})	1461.942
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.960(1)
b (Å)	12.084(5)
c (Å)	13.696(6)
α (°)	73.96(4)
β (°)	84.69(4)
γ (°)	80.93(4)
V (Å^3)	1405.5(9)
Z	1
D_x (mg m^{-3})	1.73
μ (Mo Kα) (cm^{-1})	9.14
$F(000)$	740
Observed reflections	$4004(I > 3\sigma(I))$
Final R	0.073
Final R_w	0.079

Analyses

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

Physical measurements

The 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}. Cross-polarization magic angle spinning (CP/MAS) $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian Unity 300 spectrometer operating at 7.0 T (^{13}C at 75 MHz) using high-power proton decoupling. The thermal measurements were made in a Mettler TA 3000 equipment. TG curves were obtained by heating samples of the corresponding complex in a pure air atmosphere at a heating rate of 10 °C min^{-1}. The conductivity of 10^{-3} M solutions in water was measured at 25 °C on a Radiometer Copenhagen CDM 83 conductometer (cell constant 0.9).

X-ray structure determination

The refined cell constants and other relevant crystal data for $[Cd_2(Cx)_4(DMSO)_2]\cdot 2H_2O$ are presented in Table 1, together with details of the intensity measurements.

White crystal, size 0.23×0.23×0.23 mm. Throughout the experiment Mo Kα radiation was used with a graphite crystal monochromator on an Enraf-Nonius CAD-4 single-crystal diffractometer ($\lambda = 0.71073$ Å). The unit-cell dimensions were determined from the angular settings of 25 reflections with θ between 15 and 20°. The space group was determined to be $P\bar{1}$ from structure determination. The intensity data of 5176 reflections, in the *hkl* range $(-10, -13, 0)$ to $(10, 14, 16)$ and θ limits ($0 < \theta < 25°$) were measured, using the ω–2θ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 60 min. The final drift correction factors were between 0.97 and 1.01. On all reflections profile analysis was performed [6, 7]; semiempirical absorption correction was applied, using ψ scans [8], μ(Mo Kα) = 9.14 cm^{-1} (correction factors were in the range 0.93 to 1.00). Some double measured reflections were averaged, $R_{int} = \Sigma(I\langle I\rangle)/\Sigma I = 0.012$, resulting in 4949 unique reflections of which only 4004 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values. The structure was solved by direct methods using the program SHELXS86 [9] and expanded by DIRDIF [10]. Isotropic least-squares refinement, using a local version of the program SHELX76 [11], converged to $R = 0.13$. At this stage additional empirical absorption correction was performed using DIFABS [12], resulting in a further decrease of R to 0.096. The maximum and minimum absorption correction factors were 1.45 and 0.70, respectively. Further anisotropic refinements followed by a difference Fourier synthesis allowed the location of some hydrogen atoms, the rest were geometrically placed and refined riding on their parent atom.

During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. All hydrogens were refined isotropically with a common thermal parameter. The final conventional agreement factors were $R = 0.073$ and $R_w = 0.079$ for the 4004 ‘observed’ reflections and

TABLE 2. Fractional positional and thermal parameters with e.s.d.s. in parentheses

Atom	x	y	z	U_{eq}[a] ($Å^2 \times 10^2$)
Cd(1)	0.47729(8)	0.52298(5)	0.63384(5)	3.14(2)
O(1)	0.6775(8)	0.4111(5)	0.7130(5)	4 3(2)
O(3)	0.4107(7)	0.5271(5)	0.7959(4)	3.5(2)
O(1′)	0.576(1)	0.5867(6)	0.4660(5)	6.2(3)
O(3′)	0.5905(8)	0.6838(5)	0.6278(4)	4.3(2)
O(6)	0.2522(8)	0 6474(7)	0.5995(6)	6.7(3)
N(1)	0.7144(8)	0 5928(6)	0.9639(5)	3.1(2)
N(2)	0.7567(8)	0.5117(6)	0.9135(5)	3.1(2)
C(2)	0.6608(9)	0.4927(7)	0.8545(6)	2 9(3)
C(3)	0 5057(9)	0.5508(7)	0.8452(5)	2.4(2)
C(9)	0.546(1)	0.7562(7)	1.0019(6)	3.3(3)
O(5)	0.3534(7)	0.9153(6)	1.0211(5)	4.4(2)
C(7)	0.199(1)	0.9492(9)	0.9924(8)	5.0(4)
O(4)	0.1727(7)	0.8798(5)	0.9282(5)	4.1(2)
C(5)	0.3253(9)	0.7112(7)	0.8837(6)	2.8(3)
C(4)	0.4704(9)	0.6416(7)	0.8954(5)	2.4(2)
C(10)	0.5772(9)	0.6629(7)	0.9548(6)	2.7(3)
C(8)	0.407(1)	0 8210(7)	0.9862(6)	3 3(3)
C(6)	0.3001(9)	0.7978(7)	0.9297(6)	3.0(3)
C(1)	0.725(1)	0.4014(7)	0.7984(6)	3.2(3)
O(2)	0.8223(8)	0.3206(6)	0.8421(5)	5.1(3)
C(11)	0.833(1)	0.6069(9)	1.0252(7)	4.3(4)
C(12)	0.926(1)	0.699(1)	0.9643(9)	5.8(5)
C(3′)	0.6307(9)	0.7680(7)	0.5585(6)	2.8(3)
C(2′)	0.6589(9)	0 7659(7)	0.4519(6)	2.9(3)
N(2′)	0.7009(8)	0 8560(6)	0.3807(5)	3 2(2)
N(1′)	0.7184(8)	0 9521(6)	0.4036(5)	3 1(2)
C(9′)	0.707(1)	1.0745(7)	0.5179(6)	3.3(3)
O(5′)	0 6784(9)	1.1764(5)	0.6485(5)	4.8(3)
C(7′)	0.639(1)	1.1431(8)	0.7560(7)	5.2(4)
O(4′)	0.6269(9)	1.0211(6)	0.7835(5)	5.6(3)
C(5′)	0.631(1)	0.8837(7)	0.6812(6)	3.3(3)
C(4′)	0.6560(9)	0.8723(7)	0.5800(6)	2.6(3)
C(10′)	0.6964(9)	0.9666(7)	0.4994(6)	2 8(3)
C(8′)	0.677(1)	1.0811(7)	0.6140(6)	3.4(3)
C(6′)	0.645(1)	0.9863(8)	0.6962(6)	3.6(3)
C(1′)	0 639(1)	0.6674(7)	0.4095(7)	3.6(3)
O(2′)	0.6828(9)	0.6677(6)	0.3224(5)	5.6(3)
C(11′)	0.772(1)	1.0421(8)	0.3154(6)	4.0(3)
C(12′)	0.942(1)	1.040(1)	0.3146(8)	6.0(4)
S(1)	0.1265(5)	0.5881(4)	0.5695(4)	10.6(2)
C(21)	−0.007(2)	0.581(2)	0.667(1)	10.6(8)
C(22)	0.052(2)	0.674(2)	0.469(1)	11.2(9)
O(8)	0.101(1)	0.1876(9)	0.818(1)	12.5(5)

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

TABLE 3. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Cd(1)–O(1)	2.237(6)	Cd(1)–O(3)	2.257(6)
Cd(1)–O(1′)	2.350(7)	Cd(1)–O(3′)	2.308(6)
Cd(1)–O(6)	2.319(8)	Cd(1)–O(1′A)	2.277(9)
O(1)–C(1)	1.25(1)	O(3)–C(3)	1.245(9)
O(1′)–C(1′)	1.24(1)	O(3′)–C(3′)	1.259(9)
O(6)–S(1)	1.567(9)	C(2′)–C(1′)	1.50(1)
C(2)–C(1)	1.52(1)	C(1′)–O(2′)	1.22(1)
C(1)–O(2)	1.26(1)		
O(3)–Cd(1)–O(1)	79.7(2)	O(1′)–Cd(1)–O(1)	102.2(3)
O(1′)–Cd(1)–O(3)	157.7(2)	O(3′)–Cd(1)–O(1)	88.5(2)
O(3′)–Cd(1)–O(3)	84.1(2)	O(3′)–Cd(1)–O(1′)	73.9(2)
O(6)–Cd(1)–O(1)	162.9(3)	O(6)–Cd(1)–O(3)	83.4(3)
O(6)–Cd(1)–O(1′)	92.6(3)	O(6)–Cd(1)–O(3′)	87.6(3)
O(6)–Cd(1)–O(1′A)	92.1(3)	C(3)–O(3)–Cd(1)	117.7(5)
C(1)–O(1)–Cd(1)	130.8(6)	C(3′)–O(3′)–Cd(1)	135.4(5)
C(1′)–O(1′)–Cd(1)	141.0(6)	S(1)–O(6)–Cd(1)	112.6(5)
C(2)–C(1)–O(1)	118.6(7)	O(2)–C(1)–C(2)	117.1(8)
C(2′)–C(1′)–O(1′)	117.6(8)	O(2′)–C(1′)–C(2′)	120.8(8)

404 variables. The function minimized was $\Sigma w(F_o - F_c)^2$, $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$ with $\sigma(F_o)$ from counting statistics. The maximum shift to e.s.d. ratio in the last full-matrix least-squares cycle was less than 0.7. The final difference Fourier map showed no peaks higher than 0.69 e $Å^{-3}$ or deeper than -0.70 e $Å^{-3}$. The slightly high R factor found may be assigned to crystal quality and slight disorder on the water molecules. Atomic scattering factors were taken from International Tables for X-ray Crystallography [13]. Geometrical calculations were made with PARST [14]. All calculations were made on a MicroVAX-3400 at the Scientific Computer Center of the University of Oviedo.

Final positional and thermal parameters are given in Table 2. Molecular geometry data are collected in Table 3.

Results and discussion

Description of the structure

Figure 1 shows an ORTEP [15] drawing of the complex with the atomic numbering and thermal ellipsoids.

Crystals of the compound contain dimeric $[Cd(Cx)_2(DMSO)]_2$ molecules and uncoordinated water molecules that provide crystalline stability through a network of hydrogen bond interactions. Each dimeric unit has crystallographic 1 symmetry, with the inversion center lying on the midpoint of Cd...Cd interaction, so that only a half of the complex molecule is crystallographically independent. Each dimer contains cadmium atoms bridged by two oxygens from two symmetry related carboxylate groups (O(1′), O(1′A)) with Cd(1)...Cd(1A) 3.833(2) Å ($1-x$, $1-y$, $1-z$) separations, generating planar Cd_2O_2 rhombs. The metal environment is formed by two O_{carbox} and two O_{ceto} atoms from the cinoxacinate monoanions, one oxygen of the DMSO molecule and a carboxylate oxygen atom which acts as a bridge. One of the coordinated cinoxacinate ions acts as a bidentate chelate and a bridging ligand and the other as a bidentate chelate ligand. The observed value for the Cd–Cd distance strongly suggests that no direct cadmium–cadmium bond interaction is present in this structure. The distortion of the octahedron is not severe with Cd–O bond lengths in the

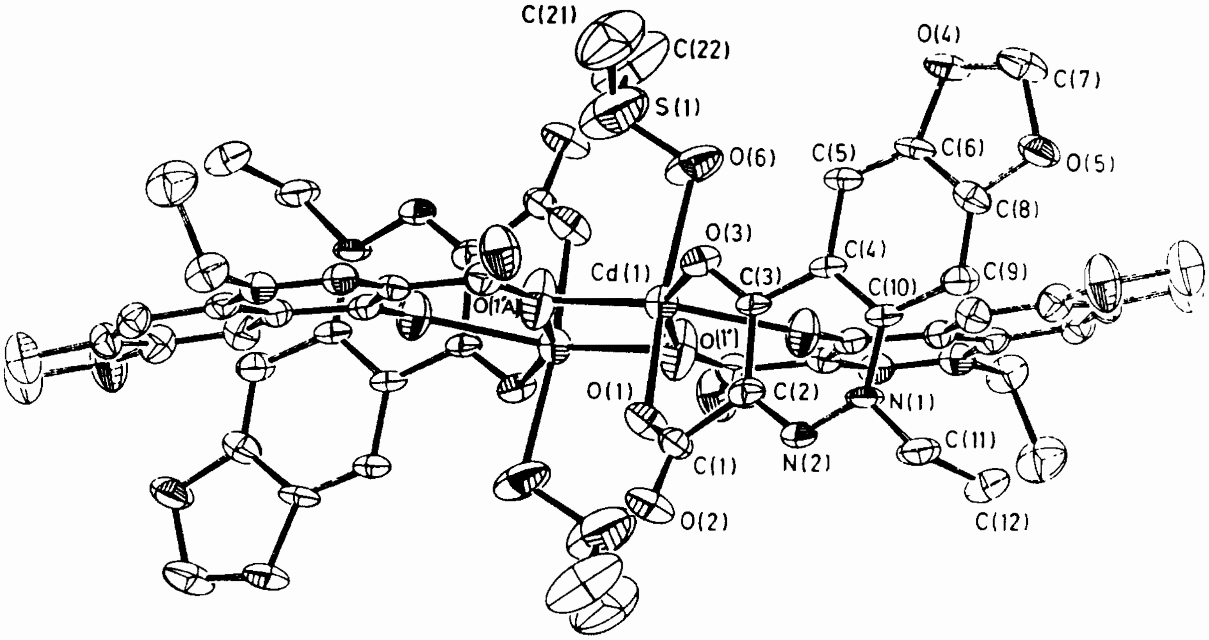


Fig. 1. ORTEP diagram showing a view of the compound and the atomic number scheme.

range 2.237(6)–2.350(7) Å and relevant angles lie between 83.4(3) and 92.6(3)°. The Cd–O_{carbox} distances are similar to those observed in compounds of related ligands [16].

Distances and angles within the cinoxacinate ion are similar to those described for the free cinoxacin [17] with the expected changes in the carboxylate group area due to its deprotonation, as already reported for the previously studied complexes [4, 5].

The three rings of each cinoxacin ligand are coplanar. The two cinoxacinate ligands linked to the Cd metal are placed in such a way that the aromatic rings systems are perpendicularly placed, forming a dihedral angle of 96.9°.

In the complex, the C(12)–C(11)–N(1)–N(2) and C(12′)–C(11′)–N(1′)–N(2′) torsion angles are both 91°. This indicates that the plane containing the two ethyl group carbon atoms is almost perpendicular to the cinoxacin ring system. This geometric fact is also observed in the crystal structure of the parent ligand and in previously reported Co(II) and Zn(II) cinoxacin complexes [4, 5].

Intermolecular hydrogen bonds with symmetry codes are given in Table 4. Figure 2 shows a PLUTO [18] drawing of the crystal packing in the solid. Interaction between dinuclear entities is made through a three-dimensional network of hydrogen bonds involving carboxylate oxygen atoms O(2) (1) and O(2′) (2), and water molecules.

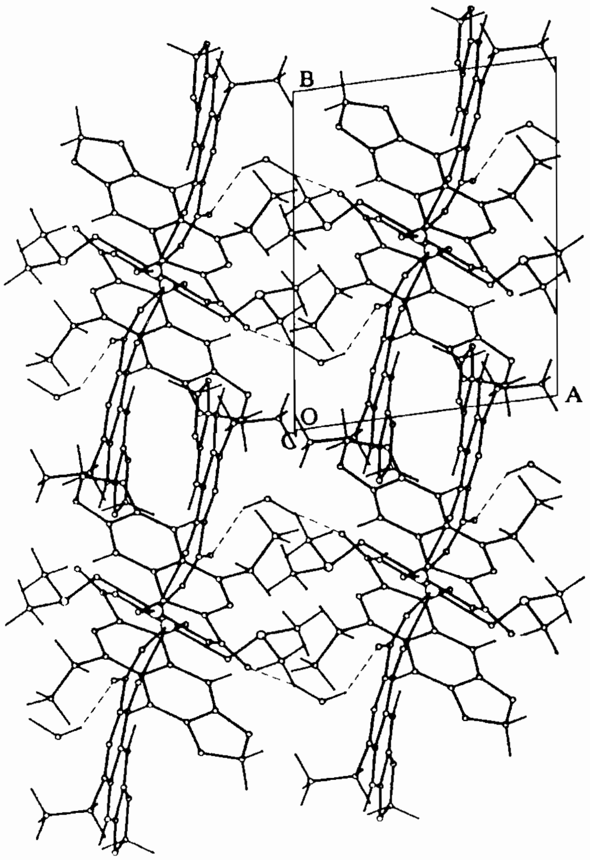


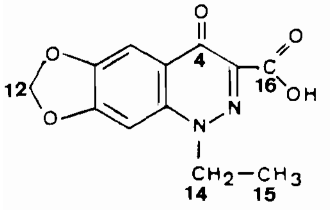
Fig. 2. PLUTO diagram showing the crystallographic packing along the *z* axis.

TABLE 4. Distances (Å) and angles (°) involved in hydrogen bridges

A–H...B	A–H (Å)	H...B (Å)	A–B (Å)	AHB (°)
O(W8)–H(W82)–O(2)	1.1(1)	1.7(1)	2.79(1)	189(11) (1)
O(W8)–H(W81)–O(2′)	0.8(1)	2.3(1)	3.00(1)	134(13) (2)

Symmetry codes: (1) $+x-1$, $+y$, $+z$; (2) $-x+1$, $-y+1$, $-z+1$.

TABLE 5. ^{13}C NMR data (ppm) of cinoxacin and its Cd(II) complexes



C	Cinoxacin	$[Cd_2(Cx)_4(DMSO)_2]\cdot 2H_2O$	$Cd(Cx)_2\cdot H_2O$
4	168.5	167.8, 170.0	167.9
12	98.5	94.5	94.0
14	55.7	53.9 (broad)	52.1
15	16.2	16.3, 12.0	13.5
16	163.9	156.5, 155.5	154.0
C_{DMSO}		38.5, 40.0	

General physicochemical characteristics of the complexes

Due to the impossibility of obtaining structural information from single crystal X-ray diffraction of compound **II**, an attempt to clarify its nature by other physical measurements was performed.

Complex **I** is well soluble in hot H_2O, and insoluble in DMSO and DMF. Complex **II** is insoluble in H_2O and very soluble in DMSO. For compound **I** conductivity measurements in water solutions resulted in a $\Lambda_{mol} = 197$ Ω^{-1} cm^2 mol^{-1}; for compound **II** the measurements in DMSO solutions gave a value of 39 Ω^{-1} cm^2 mol^{-1}. These values corresponding to a 1:1–2:1 type of electrolyte (for **I**) and 1:1 (for **II**) suggest appreciable dissociation [19, 20].

The TG curves of the complexes show three well-separated thermal events. The first (100–250 °C) corresponds to the elimination of two water and two DMSO molecules from compound **I** (found 13.6%; calc. 13.1%) and only the elimination of two water molecules from compound **II** (found 2.6%; calc. 2.7%). The second and the third steps are due to pyrolytic decomposition of cinoxacin. The final residue at 825 °C (found 17.9%; calc. 17.6%) is CdO characterized by X-ray diffraction and IR spectroscopy.

IR spectra of both compounds show as the most significant bands those at 3600–3200 cm^{-1} ν(O–H), 1650–1600 cm^{-1} ν_a(OCO)+ν(CO) and 525 cm^{-1} ν(Cd–O). As in other metal–cinoxacinate complexes [4, 5] these assignments suggest that the coordination of the ligand occurs through the O_{carbox} and O_{ceto} atoms; furthermore, the assignment of the band at 1010 cm^{-1} ($\nu(S{=}O)_{DMSO}$) in the IR spectrum of compound **I** suggests that the coordination of DMSO occurs through oxygen [21].

The ^{13}C NMR data of the ligand (HCx) and its cadmium complexes in the solid state are shown in Table 5. We can appreciate in the spectrum of the $[Cd_2(Cx)_4(DMSO)_2]\cdot 2H_2O$ complex (Fig. 3) that each carbon atom (C_4, C_{16} C_{15} and C_{DMSO}) shows two signals as a consequence of the fact that the two Cx ligands are coordinated in different ways to Cd in the asymmetric unit. Since atoms within those molecules are no longer identical, the chemical shifts may be different as well, causing extra lines to appear in the solid-state spectrum [22].

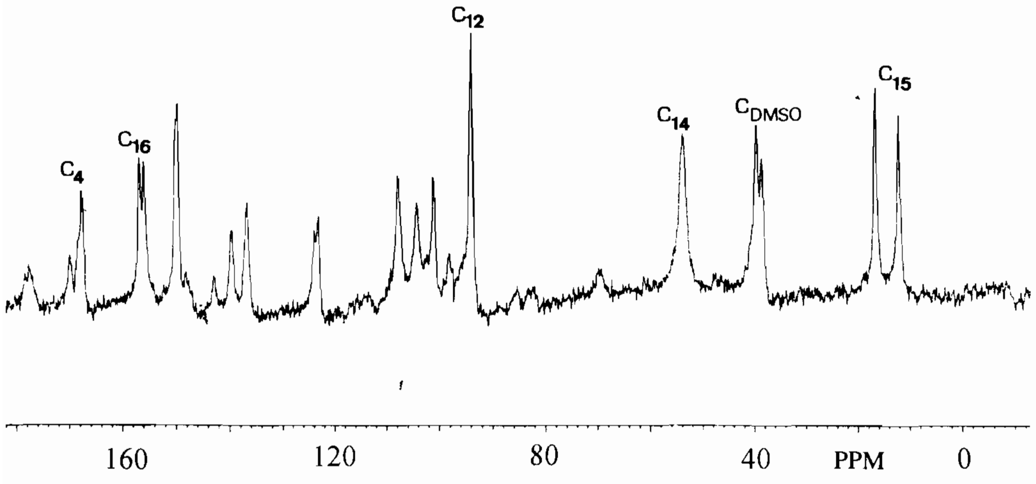


Fig. 3. ^{13}C NMR spectrum in the solid state of the $[Cd_2(Cx)_4(DMSO)_2]\cdot 2H_2O$ complex.

Supplementary material

Anisotropic thermal parameters, H-atom parameters and lists of structure amplitudes are available from the authors on request.

Acknowledgements

We thank Dr F. Estevan (University of Valencia) for the registration of the NMR spectra. Financial support from CICYT (FAR91-0197) is gratefully acknowledged.

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