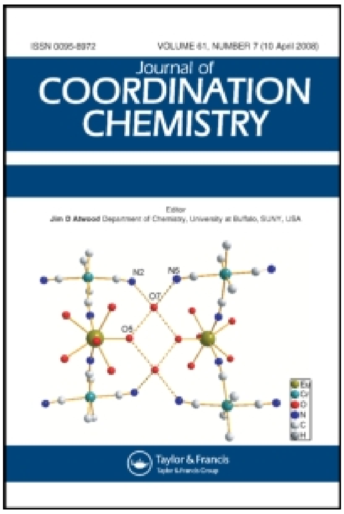

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X-RAY CRYSTALLOGRAPHIC EVIDENCE FOR ADDITION OF WATER TO NITROSODICYANOMETHANIDE IN THE 3d-METAL COORDINATION SPHERE

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In the system $M^{II}–ONC(CN)_2^- - H_2O$ ($M = Co, Ni, Cu$) nucleophilic addition of water to $ONC(CN)_2^-$ is shown to form new anionic chelate ligands. The compounds $K[CoL_2L'] \cdot 1.5H_2O$, $[NiL_2(H_2O)_2]$ and $[CuL_2]$, where $L = ONC(CN)C(O)NH_2^-$, $L' = ONC(CN)C(NH)O^{2-}$, were isolated. It was shown by X-ray crystallography that the complex $[CoL_2L']^-$ has two ligands, L, bonded through carbonyl oxygen and nitroso nitrogen, while the ligand L′ is coordinated through both imine and nitroso nitrogens.

Keywords: Nucleophilic addition; nitrosodicyanomethanide; cobalt(II); nickel(II); copper(II); X-ray structure

INTRODUCTION

In the course of a systematic study of nucleophilic additions to non-linear pseudohalides in the coordination sphere of transition metal atoms,[1] we recently paid attention to the nitrosodicyanomethanide anion. This anion is considerably more reactive in comparison with tricyanomethanide or dicyanamide and forms with methanol in the coordination sphere of several transition metals anionic chelate ligands, *viz.* methyl 2-cyano-2(hydroximino)ethanimidate.[2,3]

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It is well known that nitrosodicyanomethanide in aqueous solution enters into a hydrolytic reaction, which is accelerated in the presence of 3d ions, e.g., Co^{2+}, Ni^{2+}, Cu^{2+}.[4] In these systems, nucleophilic addition of water to nitrosodicyanomethanide in the 3d coordination sphere is supposed. Therefore, we aimed at a study of products isolated from the systems $M(NO_3)_2–KONC(CN)_2–H_2O$ ($M = Co, Ni, Cu$). X-ray crystallography of $KCo\{ONC(CN)_2\}_3 \cdot 4.5H_2O$ showed that the Co atom is bonded to two different anionic ligands formed by the nucleophilic reaction mentioned; these ligands are $ONC(CN)C(O)NH_2^- = L$, $ONC(CN)C(NH)O^{2-} = L'$. In the present note, results of this study, as well as IR and electronic spectroscopic data for the compounds obtained are given.

EXPERIMENTAL

Preparation

The solutions formed from $M(NO_3)_2$ ($M = Co, Ni, Cu$), $KONC(CN)_2$ and water in the mol ratio 1 : 2.5 : 300 exhibit striking colour changes and after several days standing, orange-red (Co^{III}), rose-red (Ni^{II}) and green (Cu^{II}) crystals were isolated. All three prepared compounds gave good analytical results for C, H, N and metal. The Co^{III} and Ni^{II} compounds lose water at 150 and 140°C, respectively, and the chelates decompose at 300°C; the Cu^{II} chelate decomposes at 220°C. Skopenko *et al.*, prepared $[NiL_2(H_2O)_2]$ and $[CuL_2]$, but using $KONC(CN)C(O)NH_2$ and respective metal nitrates as starting materials.[5]

Crystal Data for $K[CoL_2L'] \cdot 1.5H_2O$

A total of 1727 intensity data having $F_0 > 4\sigma(F_0)$ and $2 < \theta < 23°$ was collected by the $\theta–2\theta$ scan method on an Enraf-Nonius CAD4 diffractometer with $\lambda = 0.71069$ Å for MoK_α radiation at $T = 298$ K. The structure was solved by the Patterson method and subsequent Fourier syntheses using SHELXS86.

Refinement was made by full-matrix least-squares SHELXL93 software to an R_1 value of 0.030. Non-hydrogen atoms were treated anisotropically except for the disordered water oxygen atoms. Hydrogen atom positions were located from difference maps and constrained at the distance N–H of 0.86 Å with $U(H) = 1.2U_{eq}(N)$. Final atomic positions are given in Table I.

TABLE I Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	$U(eq)$
Co(1)	2944(1)	2163(1)	952(1)	22(1)
O(2)	4659(2)	1776(3)	868(1)	26(1)
C(3)	4824(3)	2192(4)	300(2)	25(1)
C(4)	3745(3)	2829(5)	−187(2)	26(1)
N(5)	2697(2)	2873(4)	30(1)	25(1)
N(6)	5904(3)	2034(4)	141(2)	38(1)
C(7)	3749(3)	3429(6)	−842(2)	42(1)
N(8)	3728(3)	3985(7)	−1361(2)	72(1)
O(9)	1691(2)	3416(3)	− 347(1)	35(1)
O(10)	2519(2)	−301(3)	722(1)	26(1)
C(11)	1392(3)	−670(4)	731(2)	24(1)
C(12)	649(3)	817(4)	884(2)	26(1)
N(13)	1249(2)	2377(4)	969(1)	26(1)
N(14)	928(3)	−2272(4)	590(1)	32(1)
C(15)	−623(3)	709(5)	935(2)	30(1)
N(16)	−1637(3)	674(5)	977(2)	50(1)
O(17)	726(2)	3811(3)	1059(1)	37(1)
N(18)	3365(3)	1622(4)	1872(1)	29(1)
C(19)	3752(3)	2960(5)	2281(2)	35(1)
C(20)	3721(3)	4675(5)	1904(2)	31(1)
N(21)	3350(2)	4534(4)	1258(1)	25(1)
O(22)	4130(3)	2918(4)	2892(1)	63(1)
C(23)	4087(3)	6348(6)	2216(2)	38(1)
N(24)	4389(4)	7676(5)	2473(2)	58(1)
O(25)	3272(2)	5864(3)	864(1)	32(1)
K(1)	886(1)	4645(2)	−1739(1)	65(1)
OW1	1663(12)	3436(29)	−2874(6)	98(3)
OW2	1521(15)	4485(31)	−2925(7)	93(5)
OW3	2139(18)	5580(31)	−2678(10)	99(5)
OW4	1982(26)	2279(45)	−2820(12)	94(6)
OW5	1911(28)	1520(43)	−2484(15)	94(8)
OW6	2363(48)	6410(80)	−2385(27)	92(12)

Spectroscopic Measurements

IR spectra[3] and solid state electronic spectra[6] were obtained as described in the quoted papers.

RESULTS AND DISCUSSION

Crystals of $K[CoL_2L'] \cdot 1.5H_2O$ are monoclinic, space group $P2_1/n$ (No. 14), $a = 10.982(2)$, $b = 7.436(10)$, $c = 20.592(3)$ Å, $\beta = 102.81(1)°$, $Z = 4$, $D_c = 1.864\ \mathrm{g\,cm^{-3}}$. Some important bond lengths and angles are listed in Table II.

TABLE II Selected bond lengths (Å) and angles (°) with esds in parentheses

Co1–O2	1.951(2)	K1–N8	3.084(4)
Co1–N5	1.930(3)	K1–O9	2.952(2)
Co1–O10	1.923(2)	K1–O17^{a}	2.741(2)
Co1–N13	1.876(3)	K1–O22^{b}	2.697(4)
Co1–N18	1.892(3)	K1–N24^{c}	2.849(4)
Co1–N21	1.892(3)	K1–OW1	2.81(1)
O2–C3	1.259(4)	K1–OW2	2.69(1)
C3–C4	1.452(5)	K1–OW3	2.70(2)
C4–N5	1.325(4)	K1–OW4	3.27(3)
N5–O9	1.267(3)	K1–OW5	3.13(3)
C3–N6	1.305(4)	K1–OW6	2.66(5)
C4–C7	1.422(5)		
O10–C11	1.272(4)		
C11–C12	1.450(5)		
C12–N13	1.326(4)		
N13–O17	1.245(3)		
C11–N14	1.303(4)		
C12–C15	1.426(5)		
N18–C19	1.312(4)	O2–Co1–N5	83.2(1)
C19–C20	1.490(5)	O10–Co1–N13	84.2(1)
C20–N21	1.306(4)	N18–Co1–N21	83.0(1)
N21–O25	1.270(3)	O2–Co1–N13	174.7(1)
C19–O22	1.234(4)	N5–Co1–N18	173.2(1)
C20–C23	1.417(3)	O10–Co1–N21	174.7(1)

Symmetry codes: a: $-x, 1-y, -z$; b: $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; c: $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$.

The crystal structure consists of $[CoL_2L']^-$ anions and potassium cations, connected by donor oxygens and nitrogens from anions to form a three-dimensional network. In the $[CoL_2L']^-$ anion (Figure 1) the central Co^{III} atom is *pseudo*-octahedrally coordinated by three nitrosocarbamoylcyanomethanide ligands in chelate fashion. These have arisen from nitrosodicyanomethanide by nucleophilic addition of a water molecule to a nitrile carbon with simultaneous transfer of both protons to nitrile nitrogen in the cobalt coordination sphere. Two of the ligands formed are bidentates bonded through carbonyl oxygen and nitroso nitrogen atoms. The third ligand, after deprotonization, is coordinated through both imine and nitroso nitrogens. The intracomplex reaction is connected with oxidation of Co^{II} to Co^{III}, most likely by air. The interatomic distance C19–O22 of 1.234(4) Å is close to a double bond value and is in a good agreement with values $C(sp^2)-O = 1.362$ Å and $C(sp^2)=O = 1.230$ Å.[7] C19–C20 [1.490(5) Å] is a single bond, different, because of delocalization, to the bonds C3–C4 [1.452(5) Å] and C11–C12 [1.450(5) Å]. The potassium cation is coordinated by three oxygens (O9, O22, O24) and two nitrogens (N8, N14) from chelate ligands, and by oxygens from disordered water molecules with distances from 2.66(5) to 3.27(3) Å.

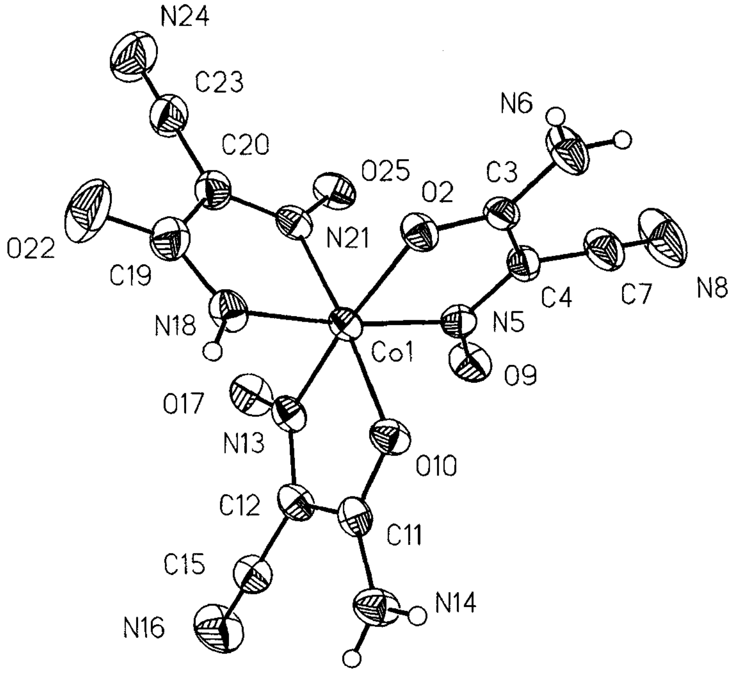

FIGURE 1 ORTEP drawing of $[CoL_2L']^-$ with 50% probability thermal ellipsoids.

Skopenko *et al.*, reported X-ray crystallographic data for $[NiL_2(H_2O)_2]$.[8] The central Ni^{II} atom is *trans*-coordinated by nitroso N and carbonyl O donors from two nitrosocarbamoylcyanomethanides in the equatorial plane, and this group is completed by two water molecules in axial sites to form a distorted octahedron.

In the IR spectra of the compounds under investigation bands were tentatively assigned, as given in the Table III. The main characteristics are bands of $\nu(C{\equiv}N)$, $\nu(C{=}O)$, $\nu(NH_2)$, $\delta(NH_2)$, and $\nu(ONC)$ vibrations, as well as those of skeletal ν(M-donor) modes. The $\nu(OH_2)$ modes (when water is present) are revealed as shoulders on the high-frequency side of intense $\nu_{as}(NH_2)$ bands. In the region *ca* 700–400 cm^{-1} many weak to medium intensity bands occur, probably ring deformation in origin (not included in Table III), and therefore potential water deformation or libration bands cannot be identified.

The electronic spectrum of $K[CoL_2L'] \cdot 1.5H_2O$ exhibits two spin-allowed *d–d* bands at 1.89 and 2.65 μm^{-1}, which can be assigned to the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{2g} \leftarrow {}^1A_{1g}$ transitions, respectively, in O_h symmetry (neglecting the

TABLE III Important vibration frequencies (cm^{-1}) for the chelate complexes

$K[CoL_2L'] \cdot 1.5H_2O$	$[NiL_2(H_2O)_2]$	$[CuL_2]$	*Assignment*
3478sh, br	3450sh		$\nu(OH_2)$
3366vs	3364vs	3331vs	$\nu_{as}(NH_2)^a$
3326sh			
3240sh	3246sh	3237vs	$\nu_s(NH_2)$
3196vs	3198vs	3115sh	
2226ms	2228ms	2234ms	$\nu(C{\equiv}N)$
1669vs	1668vs	1653vs	$\nu(C{=}O)$, $\nu(C{=}C)$
1586ms	1586ms	1566s1547sh	$\delta(NH_2)$, $\delta(CNH)$
1467sh	1468sh	1485vw	$\nu_{as}(ONC)$
1453ms	1454ms		
1399vs	1398vs	1402vs	$\nu_s(ONC)$
1281vs	1302vs	1338s	$\nu(C{-}N)$, $\nu(C{-}O)$
1171vs	1178vs	1190ms	$\nu(C{-}C)$
1103ms	1103ms	1080m	
771m	769m	765w	$\rho_w(NH_2)$
410sh	297w	328m	ν(M-donor)
392m	272mw	291m	
373sh	235m	233m	
336w			
290w			

[a] The band for the Co^{III} chelate can include $\nu(NH)$.

distortion of the octahedron). The spectrum of $[NiL_2(H_2O)_2]$ has two spin-allowed octahedral bands, ${}^3T_{2g} \leftarrow {}^3A_{2g}$ and ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$, at 1.06 and 1.94 μm^{-1}, respectively. The third band, ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$, is hidden under an intense CT absorption. The compound $[CuL_2]$ shows two *d–d* bands at 1.62 and 2.17 μm^{-1}, which indicate a square planar structure, without any axial interaction.[9] This structure is unambiguously formed by two bidentate chelate ligands L, coordinated to copper(II) in the equatorial plane, similar to $[NiL_2(H_2O)_2]$.[8]

All three chelates show in the range *ca* 2.1–2.5 μm^{-1} peaks, which can be attributed to an intra-ligand transition, apparently to the π^* orbital.

Full lists of crystallographic data are available from the authors upon request.

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