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SYNTHESES, CHARACTERIZATION, AND MOLECULAR STRUCTURES OF NITROALKANOATO NICKEL(II), ZINC(II), AND CADMIUM(II) COMPLEXES WITH TETRAAZACYCLOALKANES

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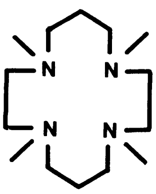
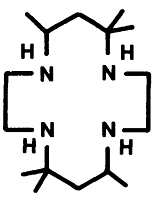
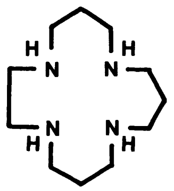
Nickel(II), zinc(II), and cadmium(II) complexes of tetraazacycloalkane (L) (L = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L^1), 7RS,14RS-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L^2), or 1,4,8,12-tetraazacyclopentadecane (L^3)) react with nitroalkanes ($RR'CHNO_2$: R = R' = H; R = H, R' = CH_3; R = R' = CH_3) in the presence of NEt_3 to afford the nitroalkanoato complexes, $[M(L)(O_2NCRR')]^+$, which have been characterized by IR, ^1H and ^{13}C NMR spectroscopy, and by X-ray analyses on three compounds.

The α-hydrogen of nitroalkane $RR'CHNO_2$ is known to be acidic and the nitroalkanoate ion, $RR'CNO_2^-$, resulting from deprotonation in a basic medium, is a potential ligand to form metal complex. A few copper1) and ruthenium2) complexes with chelated nitroalkanoate ion through both oxygens have been reported as well as M-C bonded nitromethyl complexes of platinum3) and cobalt.4)

We report here the chelating ability of nitroalkanoate ion through a series of its complexes of Ni^{2+}, Zn^{2+}, and Cd^{2+} with certain tetraazamacrocyclic ligands (L), which are able to coordinate to metal ion in folded cis-conformation.


L^1


L^2


L^3

The nitroalkanoato complexes, $[M(L)(O_2NCRR')]ClO_4$ were obtained via either route A or B in neat nitroalkane at 40 °C (Scheme 1).

A. $[ML](ClO_4)_2 + RR'CHNO_2 + NEt_3 \longrightarrow [ML(O_2NCRR')]ClO_4 + HNEt_3ClO_4$

B. $[ML(O_2CX)]ClO_4 + RR'CHNO_2 \longrightarrow [ML(O_2NCRR')]ClO_4 + CO_2 + HX$

$RR'CHNO_2 = CH_3NO_2$, $CH_3CH_2NO_2$, or $(CH_3)_2CHNO_2$

$ML^{2+} = Ni(L^1)^{2+}$, $Ni(L^2)^{2+}$,[5] $Ni(L^3)^{2+}$,[6] $Zn(L^1)^{2+}$ or $Cd(L^1)^{2+}$

$X^- = OCH_3^-$,[7] or OH^- [8]

Scheme 1.

In route A, certain ligands (L^2, L^3) are subject to nitrogen atom inversion[9,10] such that the macrocycle can not achieve the required folded conformation for nitroalkanoato chelation, and, in addition, a considerable amount of $HNEt_3ClO_4$ is formed. Therefore careful product purification was required. On the other hand, the reaction through route B proceeds nicely and the nitroalkanoato complexes were isolated cleanly.

Elemental analyses (C,H,N) of 12 compounds out of 15 listed in Scheme 1 were consistent with $[M(L)(O_2NCRR')]ClO_4$. The remaining three compounds, nitromethanoato complexes with L^1, were obtained as mixtures of unknown by-products which were difficult to be removed. The IR band of ν_{NO} appeared in the region of 1585 - 1595 cm^{-1} for the nitromethanoato complexes, in the region of 1603 - 1620 cm^{-1} for the nitroethanoato complexes, and in the region of 1620 - 1630 cm^{-1} for the nitropropanoato complexes, respectively. The selected data of ^1H and ^{13}C NMR spectra for the Zn and Cd complexes are shown in Table 1.

X-Ray structural analyses[11] were carried out on $[Ni(L^2)(O_2NCH_2)]ClO_4 \cdot 1/2H_2O$ (**1**),[12] $[Ni(L^1)(O_2NCH(CH_3))]ClO_4$ (**2**),[13] and $[Zn(L^1)(O_2NC(CH_3)_2)]ClO_4$ (**3**).[14] Figure 1 shows a perspective view of $[Ni(L^2)(O_2NCH_2)]^+$ along with molecular dimensions of the NiO_2NCH_2 moiety. The Ni atom is in a pseudooctahedral geometry with the macrocyclic ligand folded. The $CH_2NO_2^-$ ligand is chelated to nickel(II) through its two oxygen atoms. The C(L)-N(L) distance is shortened to 1.27 Å as compared with a normal C-N single bond. Four atoms, O(1), O(2), N(L), and C(L) are coplanar. Coordination structures of the nitroethanoato and the 2-nitropropanoato ions in **2** and **3** are similar to that of the nitromethanoato ligand in **1**.

On the basis of the crystallographic and other spectroscopic measurements presented, we firmly believe that the nitroalkanoato ligand deserves to be placed with other well-known ligands such as acetates, nitrates, and carbonates in this particular system.

Table 1. Selected ^{1}H and ^{13}C NMR data of nitroalkane and nitroalkanoato complexes of $Zn^{II}(L^{1})$ and $Cd^{II}(L^{1})$ in $CDCl_3$ $^{a)}$

	^{1}H		^{13}C	
	$C\text{-}\underline{H}_3$	$NC\underline{H}R'$	$C\text{-}\underline{C}H_3$	$N\underline{C}RR'$
Nitromethane		4.33^{s}		61.4
Nitroethane	1.59^{t}	4.43^{q}	10.6	70.4
2-Nitropropane	1.56^{d}	4.66^{se}	19.1	79.1
$[ZnL^{1}(O_2NCH_2)]ClO_4$		5.68^{s}		98.7
$[ZnL^{1}(O_2NCH(CH_3))]ClO_4$	1.83^{d}	6.00^{q}	13.0	106.7
$[ZnL^{1}(O_2NC(CH_3)_2)]ClO_4$	1.85^{s}		18.5	114.1
$[CdL^{1}(O_2NCH_2)]ClO_4$		5.74^{s}		99.2
$[CdL^{1}(O_2NCH(CH_3))]ClO_4$	1.85^{d}	6.05^{q}	13.4	107.7
$[CdL^{1}(O_2NC(CH_3)_2)]ClO_4$	1.98^{s}		19.0	115.0

a) TMS internal standard. Superscripts, s, d, t, q, and se stand for singlet, doublet, triplet, quartet, and septet, respectively.

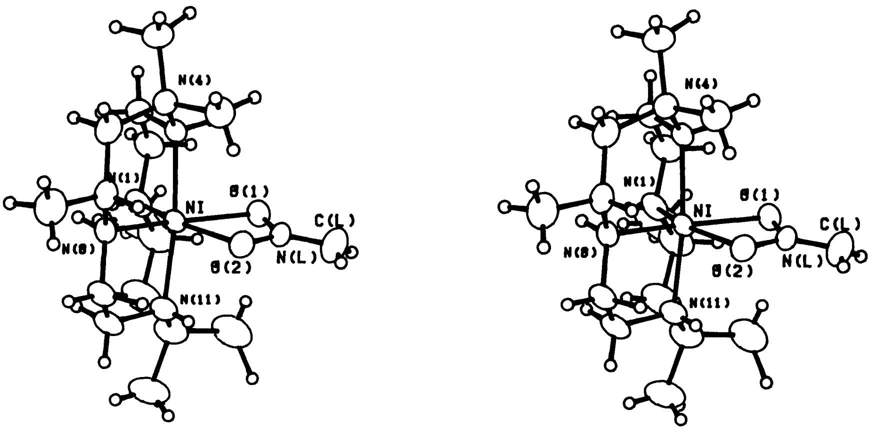


Fig. 1. Perspective view of $[Ni(L^{2})(O_2NCH_2)]^{+}$.
Bond lengths: Ni-O(1)=2.100(4), Ni-O(2)=2.100(4), O(1)-N(L)=1.305(7), O(2)-N(L)=1.312(7), N(L)-C(L)=1.273(9) Å. Bond angles: O(1)-Ni-O(2)=62.8(2), Ni-O(1)-N(L)=91.8(3), Ni-O(2)-N(L)=91.6(3), O(1)-N(L)-O(2)=113.5(4), O(1)-N(L)-C(L)=123.3(7), O(2)-N(L)-C(L)=123.2(6) °.

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5) α-Isomer (1RS,4RS,8RS,11RS-form of 7RS,14RS-L^2), see Ref. 9.

6) There are several isomers arizing from the combination of secondary amine nitrogen configurations, see Ref. 10. The isomer used in this study is that obtained from $[Ni(L^3)(en)](ClO_4)_2$ (en = ethylenediamine) by $HClO_4$-decomposition, but its nitrogen configurations have not been determined.

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11) Structural details will be reported elsewhere.

12) Violet needle crystal, $NiClO_6N_5C_{17}H_{38}\cdot 1/2H_2O$, FW = 511.68, monoclinic $P2_1/c$, a = 17.082(2), b = 9.362(1), c = 15.759(2) Å, β = 100.32(1)°, U = 2479.4(5) $Å^3$, Z = 4, Dc = 1.37 g cm^{-3}, R = 0.060 for 2576 independent reflections (2θ < 50°).

13) Blue green prismatic crystal, $NiClO_6N_5C_{16}H_{36}$, FW = 488.64, monoclinic $P2_1/n$. Diffraction data at 184 K, a = 13.344(3), b = 12.262(2), c = 14.052(3) Å, β = 107.39(1)°, U = 2194.2(7) $Å^3$, Z = 4, Dc = 1.48 g cm^{-3}, R = 0.041 for 3843 independent reflections (2θ < 55°).

14) White block, $ZnClO_6N_5C_{17}H_{18}$, FW = 509.35, monoclinic $P2_1/n$, a = 8.531(2), b = 16.887(2), c = 16.826(2) Å, β = 101.61(2)°, U = 2374.4(7) $Å^3$, Z = 4, Dc = 1.43 g cm^{-3}, R = 0.043 for 2767 independent reflections (2θ < 55°).

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