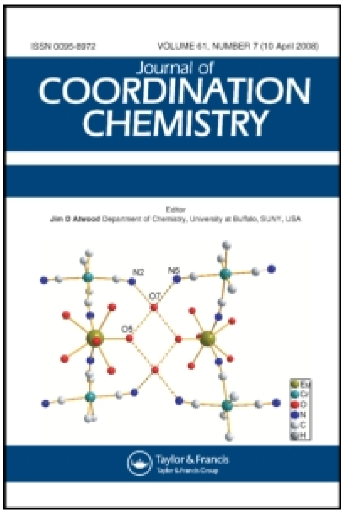

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Demetallation of a Ni(II) tetraazamacrocyclic complex by cyanoxime resulting in the formation of a stereospecific trinuclear compound $[Na(H_2O)_6]^+[NaNi_2L_6]^-$ (L = NC-C(NO)-C(O)NH)

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DEMETALLATION OF A Ni(II) TETRAAZAMACROCYCLIC COMPLEX BY CYANOXIME RESULTING IN THE FORMATION OF A STEREOSPECIFIC TRINUCLEAR COMPOUND $[Na(H_2O)_6]^+[NaNi_2L_6]^-$ ($L = NC\text{-}C(NO)\text{-}C(O)NH_2^-$)

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The reaction between the $NiA(ClO_4)_2$ and $NaHL_2$ {where $A = 14ane[N_4]$, the macrocyclic ligands derived from the product of template condensation of 2,6-diacetylpyridine with aliphatic 3,3′-diaminodipropylamine, $NH_2(CH_2)_3NH(CH_2)_3NH_2$; and L = 2-cyano-2-isonitrosoacetamide anion, ACO^- (amidecyanoxime, NC-C(NO)-C(O)NH_2^-)} has led to the formation of a highly unusual trimetallic bis-[*fac*-(triscyanoximato) nickel(II)] anionic complex anion instead of the expected Ni(II) macrocyclic complex with coordinated cyanoxime ligands. Two equivalent and symmetric trigonal-prismatic NiL_3^- units are connected to form the $[NaNi_2L_6]^-$ anion by the presence of a central sodium cation. The latter is located between two NiL_3^- anions and has an octahedral NaO_6 geometry comprised of oxygen atoms of the nitroso group of the cyanoxime ligand. The oxime ligand is planar and adopts a *cis-anti* configuration in the complex.

Keywords: Cyanoximes; Nickel(II); X-ray analysis

INTRODUCTION

Nickel(II) complexes with oximes have a long and interesting history due to their application in analytical chemistry [1–5]. Despite the simplicity of the ONC-fragment in these ligands, several binding modes of the oximes to nickel(II) centers have been established [6–15]. This investigation represents part of the program of the studies of ampolydentate cyanoxime ligands [16–19], compounds that have the general formula NC-C(NOH)-R, where R is an electron withdrawing group. Cyanoximes form a variety of coordination compounds with interesting properties [20–26]. Several

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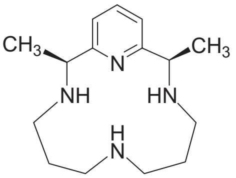
cyanoximes, such as 2-cyan-2-isonitrosoacetamide (later HACO, or amidecyanoxime), 2-cyan-2-isonitrosothioacetamide (later HTCO or thioamidecyanoxime) and their *N*,*N*-dimethylamide derivatives, previously have shown biological activity such as pesticide detoxifying [27,28], growth regulation [29–32] and anti-microbial [33,34]. Cyanoximates of copper(II) and nickel(II) displayed rather promising anti-microbial activity as well [35–37]. However, the solubilities of these compounds, as well as those analogous complexes with other cyanoxime ligands in aqueous and alcohol solutions are poor, hindering further development of the compounds for potential biomedical applications. Cyanoxime anions in transition metal complexes exhibit bidentate chelate coordination with formation of five-membered metallocycles [38–42]. The majority of transition metal cyanoximates represent neutral complexes with poor solubility in common solvents. Synthesis of coordination compounds, in which cyanoxime anions adopt a monodentate binding mode with transition metal ions, might greatly improve the solubility, essential for the delivery of the biologically active ligands into the cell [43–45].

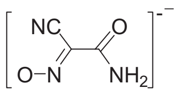
Previously we have tried to use neutral ligands such as 2,2′-bipyridyl (bipy) and aliphatic tetramine (2,3,2-tet) to design complexes in which there is the possibility for monodentate coordination of cyanoximate anions. For example, in the complexes $Cu(bipy)_2Br_2$ and $Ni(2,3,2\text{-tet})(ClO_4)_2$, four out of six coordination sites are occupied by neutral nitrogen-containing bases strongly bound to transition metals. Bromide and perchlorate anions in these compounds can be substituted with cyanoximes. Thus, the latter two complexes were used in an attempt to prepare complexes incorporating cyanoxime ligands [46–48]. The results are shown in Scheme 1 and evidence the remarkable potential of cyanoximate anions for bidentate coordination to the transition metal center despite the presence of other strongly bound ligands in the starting compounds. The HTCO thioamide ligand mentioned above and its *N*,*N*′-dimethyl analog, HTDCO, were used in these attempts (Scheme 1).

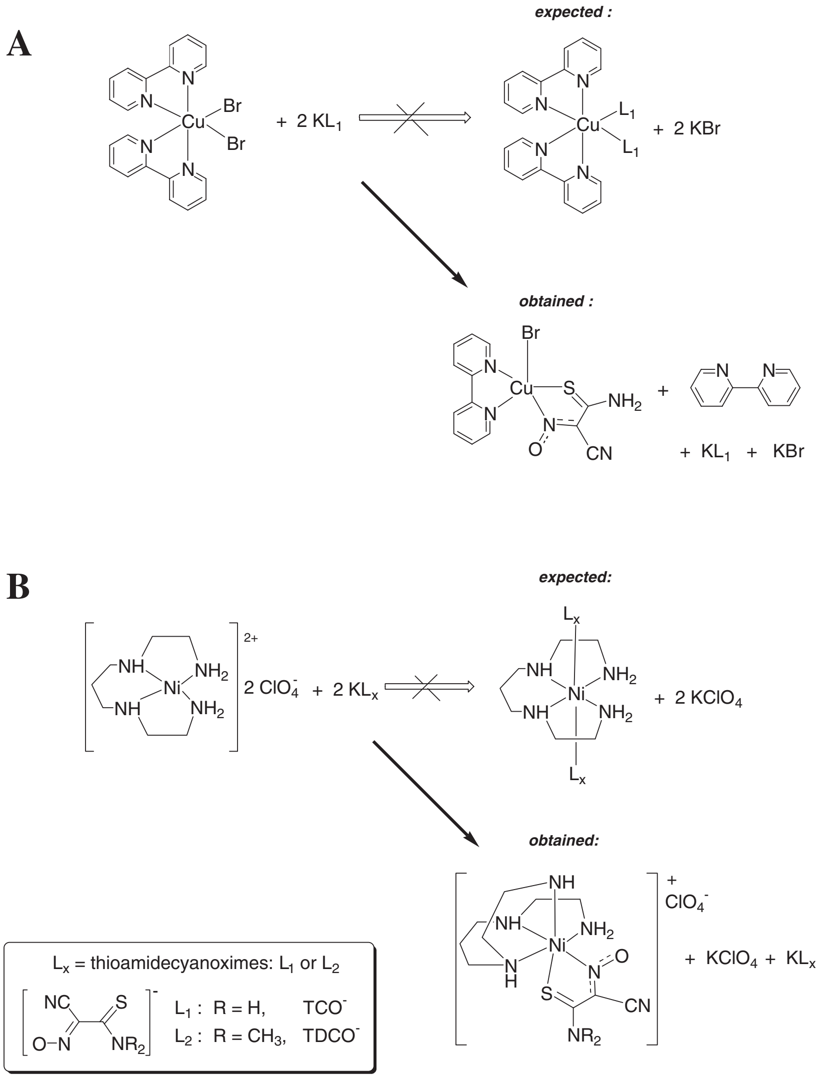
Cyanoxime anions have displaced one of the two strong donor ligands such as bipy in one complex [46], (Scheme 1, A) and promote the adoption of a rare and unfavorable *cis*-β conformation by the linear tetramine ligand 2,3,2-tet [47,48] in the other two complexes (Scheme 1, B). One terminal nitrogen atom of the aliphatic amine in these compounds was moved off the plane of the four nitrogen atoms usually observed in 2,3,2-tet complexes [49]. Therefore, it was decided to explore the use of a more rigid transition metal macrocyclic complex to achieve monodentate coordination of cyanoxime ligands. The rationale behind using tetraazamacrocyclic metal complexes was in their great stability in solution and adoption of a geometry that favors coordination of other ligands at axial positions in six-coordinate complexes. The Ni(II) diperchlorate complex with the 14ane[N_4] tetraazamacrocyclic ligand **A** below, derived from the product of the template condensation of 2,6-diacetylpyridine and aliphatic dipropylentriamine was used for this purpose.

(A) = 14ane[N_4]
meso-form



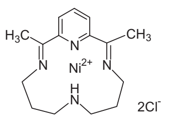
L = amidecyanoxime
ACO^-



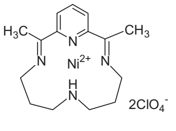


SCHEME 1

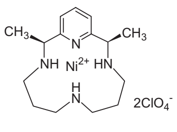
In the present study we report the synthesis of a unique Ni(II) complex **4**, shown below, using complexes **1**–**3** as precursors.



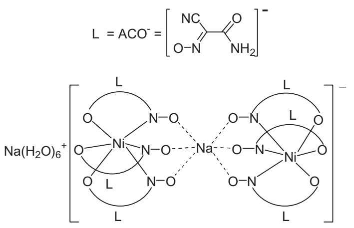
(1)



(2)



(3)



(4)

EXPERIMENTAL

Materials and Physical Measurements

Reagent or analytical grade materials were obtained from commercial suppliers (Aldrich and Malinkrodt) and were used without further purification. Elemental analyses (C, N, H) were performed by the MicroMass Laboratory of research facilities at the University of California (Berkeley). Nickel content determination was conducted by means of atomic adsorption on an AA 680U instrument (Shimadzu), calibrated with 1000 ppm $Ni(NO_3)_2$ stock solution ($pH = 1$). Melting points for organic ligands were determined using the UniMelt apparatus (by Thomas Hoover) without correction. Identification of the obtained organic compounds was carried out using ^1H, ^{13}C NMR spectroscopy (JEOL-400; $T = 296$ K; solvents $CDCl_3$ and dmso-d_6, containing internal standard TMS, by Cambridge Laboratories), and mass-spectrometry (positive FAB technique for the macrocyclic compound 14ane[N_4]; *m*-nitrobenzylic alcohol, NBA, as a matrix; and negative FAB technique for cyanoxime HACO; both methods using Autospec Q and ZAB spectrometers, Manchester, UK).

IR spectra for all synthesized compounds were recorded in KBr pellets (400–4000 cm^{-1} region at 4 cm^{-1} resolution) using a Nicolet Impact 410 spectrophotometer operating with OMNIC software. UV-visible spectra for the solutions of both ligands and several Ni(II) macrocyclic complexes were obtained on a Schimadzu SPC 2100 spectrophotometer in the range 210–850 nm at 293 K. Measurements of magnetic moments for powder samples of synthesized Ni(II) complexes were conducted at 296 K using a magnetic susceptibility balance by Johnson Matthey (Gouy method) with chromium acetylacetonate, $Cr(acac)_3$, as calibrant.

Synthesis of Compounds

Synthesis of the Ni(II) complex containing ligand **A** was conducted according to published procedures [50,51] that were slightly modified (see the *Supplementary Material*, S1). During this preparation, three different nickel(II) macrocyclic complexes **1**–**3** were isolated and characterized.

Caution! *Metal complexes containing organic ligands and perchlorate anions are potentially explosive and should be handled with care. Although we experienced no difficulties with compounds isolated as perchlorate salts, the unpredictable behavior of transition metal perchlorates necessitates extreme caution in their handling. The amount of* ClO_4^-*-containing compound used in syntheses should not exceed the relatively safe quantity of ~250 mg at a time* [52–54]. *Moreover, all obtained perchlorate complexes should not be dried in a vacuum dessicator over concentrated* H_2SO_4*. It is possible that by accident the compound and sulfuric acid may come into direct contact, leading to the generation of highly concentrated and unstable oxidizer – perchloric acid.*[1]

---

[1] A fatal accident took place at the Inorganic Chemistry division of the Chemistry Department of Kiev State University (Kiev, Ukraine) in 1963 when a graduate student N. Andreichenko died after an explosion that followed an attempt to open a stuck dessicator lid. That dessicator contained transition metals/amines/perchlorate complexes and was charged with concentrated sulfuric acid. Vials with dried substances were accidentally overturned into the acid causing generation of highly concentrated $HClO_4$ that violently interacted with organic matter and led to an explosion.

Operations with NaCN also require extreme caution and must be conducted under the protective hood at all times.

Cyanoxime Ligand

In the anionic form, 2-cyano-2-isonitrosoacetamide (ACO^-) is readily available as potassium or sodium salts, $MH(ACO)_2$ [55,56] ($M = Na^+$, K^+). Rb^+ and Cs^+ derivatives, however, exist as M(ACO) ionic compounds [57]. The syntheses of the first two salts are more practical and, using 2-cyanoacetamide and MNO_2 ($M = Na^+$ or K^+) as starting compounds, were typically carried out in aqueous solution at ~ 0°C under inert gas. Glacial acetic acid is used for HNO_2 generation in this nitrosation reaction [58], although diluted HCl and H_2SO_4 may be successfully employed as well [59]. To ensure proper nitrosation conditions, the acid was added dropwise under stirring for several hours. This is an example of the Meyer reaction [60], carried out under acidic conditions. The molar ratio between components is typically kept as follows: substituted acetonitrile/MNO_2/acid = 1 : 1.2 : 1.5. Yields are commonly in the range of 65–90%, depending on the nature of substrate-substituted acetonitrile, NC-CH_2-R [17,19,61]. Thus, the reaction of 10.0 g (0.119 M) 2-cyanoacetamide and 9.84 g (0.142 M) $NaNO_2$ in 120 cm^3 H_2O at 0°C with 10.2 cm^3 (10.7 g; 0.178 M) of glacial acetic acid after 12 h yields 11.2 g (76%) of $NaH(ACO)_2$. Extra salt (2.6 g) precipitated out in the reaction flask within 24 h at +4°C and brings the total yield of the compound to 93%. $NaH(ACO)_2$ is in the form of yellow needles. Calcd. for $C_6H_5NaN_6O_4$: C, 29.04; H, 2.03; N, 33.87. Found: C, 30.12; H, 2.54; N, 33.65%. IR spectrum: 3470, 3330 $\nu(NH_2)$; 2240 nitrile, ν(CN); 1670 ν(C=O); 1592 $\rho(NH_2)$; 1272 ν(N=O); 1170 cm^{-1} ν(CNO). UV-visible spectrum (H_2O solution): 44,000 ($\varepsilon = 13{,}100$); 35,200 ($\varepsilon = 27{,}400$); 25,000 cm^{-1} ($\varepsilon = 15$). ^{13}C NMR (D_2O solution, K_2CO_3 external standard), ppm: 165.1, amide; 128.7, central; 110.7, nitrile carbon atoms.

Acidification of aqueous solution of $NaH(ACO)_2$ by dilute HCl to pH ~3 with the subsequent saturation of the solution with solid NaCl and then extraction by ether, affords colorless protonated amide-cyanoxime HACO in ~55% yield. $R_f = 0.55$ (benzene/C_2H_5OH = 4 : 1); m.p. 176–178°C. Mass-spectrometry (negative FAB) in CH_3OH: for $C_3H_3N_3O_2$ found 113.12 (*M*). IR spectrum: 3456 ν(OH); 3378, 3336, 3230, 3178 ν_{sym}, $\nu_{asym}(NH_2)$; 2238 nitrile, ν(CN); 1707 ν(C=O); 1582 $\rho(NH_2)$; 1184 ν(N–O); 1098 cm^{-1} ν(CNO). ^1H NMR (dmso-d_6; TMS internal standard), ppm: 14.47, oxime OH; 7.91 and 7.84, amide NH_2. ^{13}C NMR (dmso-d_6; TMS internal standard), ppm: 159.7, amide; 128.1, central; 108.9, CN carbon atoms. Protonated ligand represents a stable, non-hygroscopic, source of HACO cyanoxime and can be easily converted into M(ACO) by addition of equimolar amount of base MOH ($M = K^+$, Rb^+, Cs^+, NH_4^+) or respective carbonate.

Macrocyclic Ligand A

Pure 2,12-dimethyl-3,7,11,17-tetraazabicyclo([11.3.1]heptadeca-1(17)13,15-trien), **A**, was obtained from complex **3** upon demetallation using NaCN in aqueous solutions at +65°C under basic conditions (excess NaOH). Pure tetraazamacrocycle was extracted with chloroform from the reaction mixture. Yield: 55%. The compound is a white solid sensitive towards CO_2 and moisture; m.p. 128°C. Mass-spectrometry (positive FAB): for $C_{15}H_{26}N_4$ found 263.40 ($M+1$). Both ^{1}H and ^{13}C NMR spectra of the macrocycle **A** are presented in the *Supplementary Material* (S2, S3). This compound is a stable and convenient form of the ligand that easily undergoes metallation by a variety of transition metal halides leading to stable complexes. In these typically six-coordinate complexes the tetraazamacrocyclic ligand occupies the equatorial plane leaving axial positions accessible for additional ligands to coordinate.

Complex 1

2,12-Dimethyl-3,7,11,17-tetraazabicyclo([11.3.1]heptadeca-1(17)2,11,13,15-pentaen nickel(II) diaqua dichoride. A yellow powdery compound was obtained in 60% yield. Calcd. for $C_{15}H_{26}Cl_2N_4NiO_2$: C, 42.49; H, 6.18; N, 13.21; Ni, 13.84. Found: C, 42.11; H, 6.73; N, 13.45; Ni, 14.08%. Complex **1** is diamagnetic in the solid state.

Complex 2

2,12-Dimethyl-3,7,11,17-tetraazabicyclo([11.3.1]heptadeca-1(17)2,11,13,15-pentaen) nickel(II) diperchlorate. The dark orange crystalline compound was prepared in 50% yield. Calcd. for $C_{15}H_{22}Cl_2N_4NiO_8$: C, 34.92; H, 4.30; N, 10.86; Ni, 11.38. Found: C, 35.12; H, 4.75; N, 11.05; Ni, 11.13%. UV-visible spectrum: $\lambda_{max} = 21{,}800\,cm^{-1}$ (H_2O). Compound **2** is diamagnetic in the solid state.

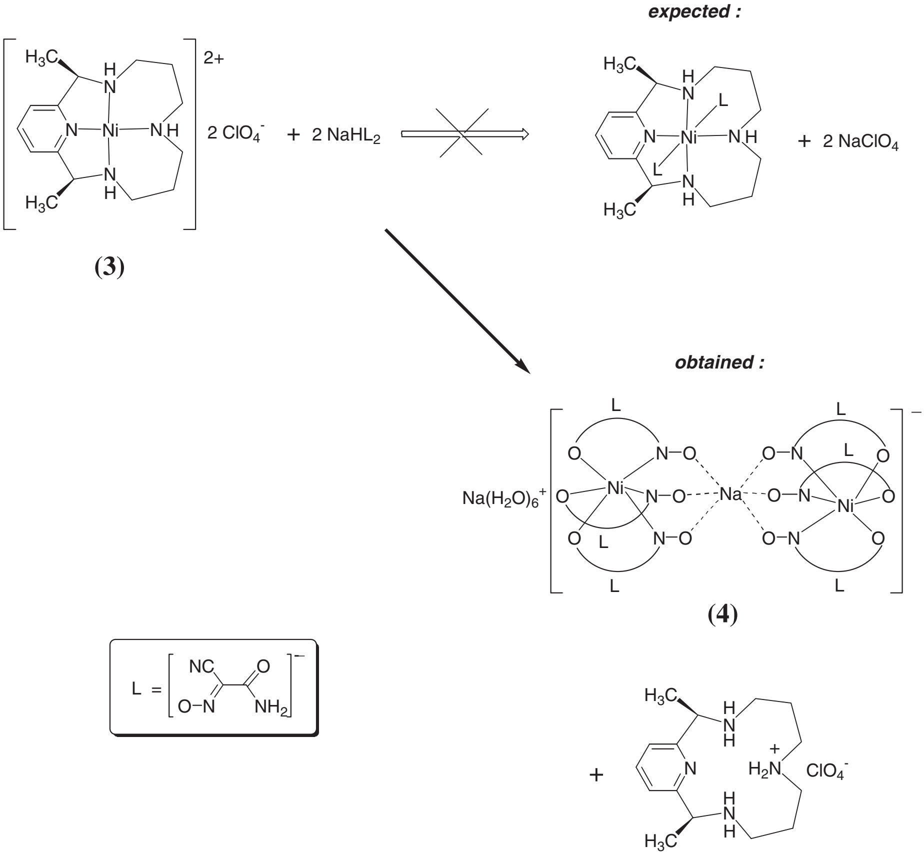
Complex 3

2,12-Dimethyl-3,7,11,17-tetraazabicyclo([11.3.1]heptadeca-1(17)13,15-trien)nickel(II) diperchlorate, contains the *meso*-form of ligand **A**. The red crystalline complex was synthesized in 65% yield. Calcd. for $C_{15}H_{26}Cl_2N_4NiO_8$: C, 34.65; H, 5.04; N, 10.77; Ni, 11.29. Found: C, 34.18; H, 5.56; N, 11.04; Ni, 11.47. UV-visible spectrum: $\lambda_{max} = 22{,}350\,cm^{-1}$ (H_2O). Complex **3** is diamagnetic in the solid state.

Complex 4

Hexaaquasodium{di-[*tris*-(2-cyano-2-isonitrosoacetamide)nickelate(II)] sodium}, $Na(H_2O)_6[Na(Ni\{ACO\}_3)_2]$. Synthesis of this compound is shown in Scheme 2. 250 mg (0.48 mM) of complex **3** was dissolved in 8 cm^3 of water at 60°C. Next, a solution containing 239 mg (0.96 mM) of $NaH(ACO)_2$ in 5 cm^3 of water was added to a solution of complex **3** at once. The color of the reaction mixture slowly changed from red to golden-brown. The volume of the resulting solution was reduced to half in the vacuum dessicator charged with KOH pellets. A brown microcrystalline precipitate, formed upon water evaporation, was filtered off and dried in a vacuum. Colorless prisms of the perchlorate salt of the demetallated ligand **A**, ($A \cdot HClO_4$), formed overnight from the mother liquor kept at +4°C. Further concentration of the solution afforded small amounts of sodium perchlorate and protonated cyanoxime HACO.

Therefore, instead of the expected macrocyclic Ni(II) cyanoximate compound, the highly unusual complex **4** was obtained in 50% yield. The brown micro-crystalline compound decomposes upon heating to ~160°C. Calcd. for $C_{18}H_{24}N_{18}Na_2Ni_2O_{18}$: C, 22.88; H, 2.54; N, 26.69; Ni, 12.50. Found: C, 23.15; H, 3.07; N, 26.12; Ni, 12.24%.



SCHEME 2

UV-visible spectrum: $\lambda_{\max} = 13{,}900\,\mathrm{cm}^{-1}$ (solid state diffusion reflectance spectra). Complex **4** is paramagnetic, $\mu_{\text{eff.}} = 3.1 \pm 0.1$ B.M. per nickel atom at 296 K. Re-dissolution of complex **4** in water with slow evaporation of the solvent afforded single crystals suitable for X-ray analysis.

X-Ray Crystal Structure Determination

A suitable brownish crystal of **4** with dimensions of $0.18 \times 0.22 \times 0.20$ mm was mounted on a Siemens R3m/V automated diffractometer for structural study. Graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used for the experiment. The lattice parameters and orientation matrix of the crystal were calculated using a least-squares procedure involving 20 reflections ($6.30° < 2\theta < 37.69°$). The crystal data and some experimental data for complex **4** are listed in Table I. Selected bond lengths and valence angles are shown in Table II. Atomic coordinates for complex **4** are presented in the *Supplementary Material* (S4). Single crystal data were collected to a 2θ limit of 45° using a variable speed $\theta/2\theta$ scanning procedure. Weights based on counting statistics and an empirical extinction correction were applied to the data.

The structure was solved using the direct method program contained in the SHELXTL-PLUS program package [62]. The final refinement and display of the

TABLE I Crystallographic data for complex **4**

Empirical formula	$C_{18}H_{24}N_{18}Na_2Ni_2O_{18}$
Formula weight	943.95
Crystal system	Rhombohedral
Space group	$R\bar{3}$/hexagonal axes
a, Å	12.909(2)
b, Å	12.909(2)
c, Å	18.165(4)
α,°	90
β,°	90
γ,°	120
Volume, $Å^3$	2621.5(8)
Z	3
T, K	293(2)
λ, Å	0.71073
$D_{calc.}/g\,cm^{-3}$	1.794
μ, cm^{-1}	1.205
$F(000)$	1440
Reflections collected (independent)	890 (768)
R (all data)	0.0435
wR^2 (all data)	0.0835

TABLE II Selected bond lengths and angles in compound **4**

Bond lengths, A		*Angles, degree*	
	anion		
N2–O3	1.301(2)	N2–C4–C5	121.5(3)
C4–N2	1.313(4)	N2–C4–C7	114.4(3)
C4–C5	1.423(5)	C5–C4–C7	123.1(3)
C4–C7	1.474(5)	N6–C5–C4	177.1(4)
C5–N6	1.147(5)	O8–C7–N9	123.0(3)
C7–O8	1.247(4)	N9–C7–C4	118.2(3)
		O3–N2–C4	119.0(3)
	coordination polyhedron[a]		
Ni1–N2	2.065(3)	N2–Ni1–N2#5	93.92(11)
Ni–O8	2.074(2)	N2–Ni1–O8#2	101.64(10)
Na1–O3	2.436(2)	N2–Ni1–O8#5	163.07(11)
Na2–O10	2.477(4)	N2#2–Ni1–O8#2	78.52(10)
		O3–Na1–O3#1	180.00
		O3–Na1–O3#2	89.36(8)
		O3–Na1–O3#4	90.64(8)

Symmetry transformations used to generate equivalent atoms:
#1: $-x, -y, -z+2$, #2: $-x+y, -z, z$ #4: $y, -x+y, -z+2$ #5: $-y, x-y, z$

[a]–symmetry related bond lengths and angles are not included.

structure was performed using the SHELXTL PC program package [63]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to N9 and O10 were located in difference maps and were refined using a riding model. Supplementary data for the structure have been deposited with the CCDC.

RESULTS AND DISCUSSION

Macrocyclic Ni(II) complexes **1** and **2** represent low-spin diamagnetic compounds with a rigid square-planar NiN_4 core. There were no interactions observed between these complexes and the cyanoximes. At the same time, macrocyclic complex **3** was found capable of coordination of two additional axial ligands with formation of tetragonal high-spin complexes [64,65]:

$$\begin{array}{lcl} [\text{NiA (Solv)}_2]^{2+} & \rightleftarrows & [\text{NiA}]^{2+} + 2\text{Solv} \\ \text{high-spin, tetragonal} & & \quad\text{low-spin, square-planar} \\ & & \quad(\text{Solv} = \text{H}_2\text{O, ROH, DMSO, DMF}) \end{array}$$

This finding was our primary objective for the synthesis of the nickel(II) macrocyclic complexes with cyanoxime anions. Despite the possibility of the formation of a complex with monodentate cyanoximes, different compounds were obtained.

The complex **4** is paramagnetic with a value of $\mu_{\text{eff.}} = 3.1$ B.M. typical for six-coordinate Ni(II) compounds. Further variable temperature magnetochemical studies were not performed for the complex because its value of $\mu_{\text{eff.}}$ did not deviate from that expected for a compound with two unpaired electrons. Complex **4** exhibits an absorption at $\sim$13,900 cm^{-1} corresponding to the second d–d transition in the UV-visible spectrum of high-spin Ni(II) compounds.

An X-ray single crystal analysis of complex **4** revealed the formation of a unique bimetallic nickel(II) complex containing ACO$^-$ anions, with no macrocyclic ligand **A** present (Scheme 2; Fig. 1). The demetallation reaction that occurred is similar to that observed for complex **3** when it was treated with an excess of NaCN (*Supplementary Material*, S1). Sodium cyanide forms a stable planar yellow anionic $Na_2[Ni(CN)_4]$ complex when the nickel ion is removed from the cavity of the macrocycle [50,51]. Contrary to that, we observed the formation of a six-coordinate tris(cyanoxime[nickelate(II)]) anion in complex **4** as a result of demetallation of complex **3** with an oxime. Macrocylic metal complexes have large formation constants and typically are very stable [76–78]. Thus, extrusion of metal ions from tetradentate macrocyclic ligands is quite rare with possible uses in preparation of metal-free macrocycles.

Crystal and Molecular Structure of Complex 4

As shown in Fig. 1, complex **4** consists of a hexaaquasodium cation, $[Na(H_2O)_6]^+$ and a rare trimetallic anion $[Na\{Ni(ACO)_3\}_2]^-$. The two sodium cations lie on three-fold inversion centers (occupancies 0.1667) and the nickel(II) cation is located on a three-fold axis (occupancy 0.3333). The Na2 exists as a six hydrated cation whereas Na1 is positioned between two symmetry related tris(cyanoxime[nickelate(II)]) units, $Ni(ACO)_3^-$. Selected bond lengths and valence angles for the cyanoxime ligand as well as the distances and angles in the coordination polyhedra of two Na$^+$ and Ni^{2+} cations are presented in Table II.

The coordination about the Na1 cation, which lies between two $Ni(ACO)_3^-$ units, can be described as octahedral because all six Na1–O3*i* (*i* = a–e) distances are 2.436(2) Å and the deviations of angles between adjacent oxygens are less than 0.5° from 90° (Table II). All six oxygen atoms which surround Na1 are from the nitroso groups of cyanoxime anions. The sodium ion of the $[Na(H_2O)_6]^+$ cation has distorted octahedral geometry with the deviations of angles from 90° approximately 3.5°. The six distances Na2–O10*i* (*i* = a–e) are 2.477(4) Å, which are slightly longer than the Na1–O3*i*

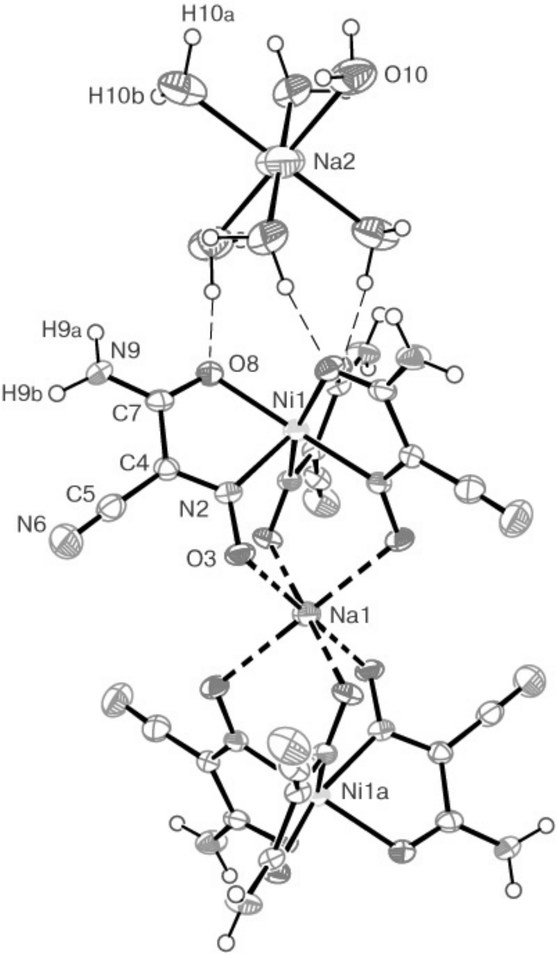


FIGURE 1 Molecular structure of complex **4** with numbering scheme for one cyanoxime ligand. An ORTEP drawing with 50% probability ellipsoids.

contacts. This difference can be attributed to the stronger interactions of the $Na1^+$ cation with oxygen atoms of NO-groups with negatively charged cyanoxime ions. All three metal centers in the complex anion $[Na\{Ni(ACO)_3\}_2]^-$ are linear with the Ni1–Na1–Ni2 angle at 180.0° and the Ni1–Na1 distance 3.715 Å.

Nickel atoms in both tris(cyanoxime[nickelate(II)]) units, $Ni(ACO)_3^-$, are six-coordinated, equivalent and have a trigonal-prismatic shape (Fig. 2). Cyanoximate anions in complex **4** exhibit bidentate chelate coordination to the transition metal center via an oxygen atom of an amide and a nitrogen atom of the nitroso group forming $[Ni(N2)_3(O8)_3]$ coordination polyhedra (Fig. 2). The "bite" angle for the N2–C4–C7–O8 chelate "claw" is 78.5°, smaller than its usual values which lie in the range 85–90°. Both $Ni(ACO)_3^-$ anionic complexes are *fac*-isomers, and their formation is determined exclusively by the coordinating role of the Na1 counter cation in the trimetallic anion $[Na\{Ni(ACO)_3\}_2]^-$. Therefore, a unique single stereospecific product of the complex **3** demetallation reaction is observed since typically, both *fac*- and *mer*-isomers are present when a complex of the MA_3B_3-type coordination polyhedron

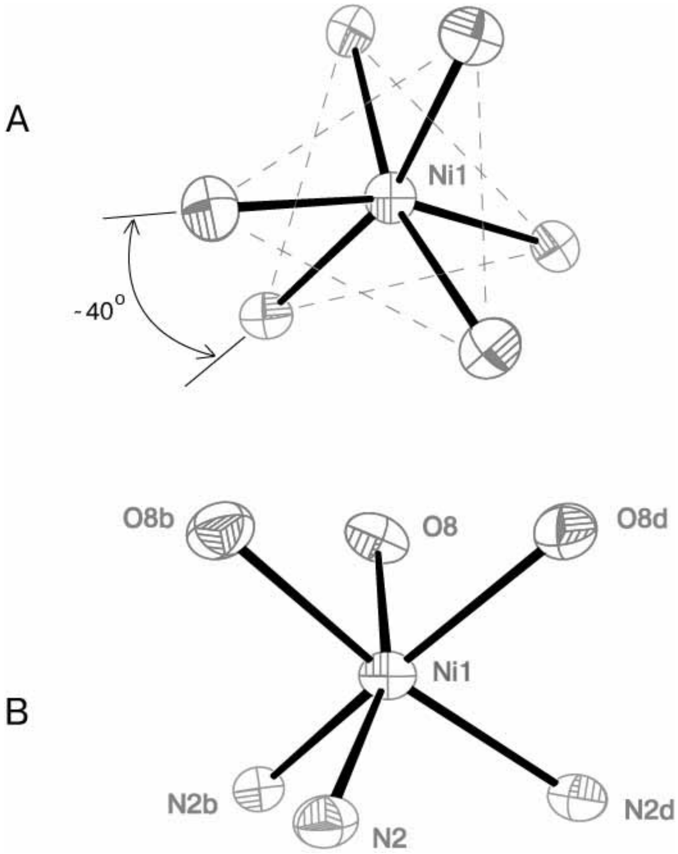
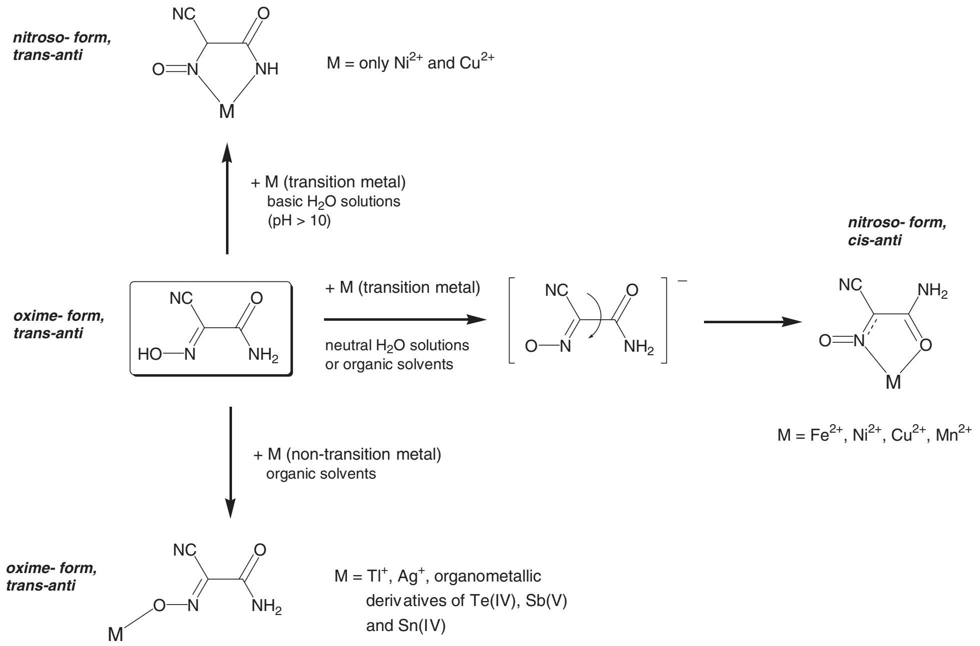


FIGURE 2 Surrounding of Ni^{2+} atoms in $\{Ni(ACO)_3\}^-$ units. A: top view showing trigonal twist angle; B: side view.

is formed [66]. Usually this is the case for *kinetically inert* hexacoordinated metal ions such as Cr^{3+}, Co^{3+}, Al^{3+}, Ru^{2+}, Rh^{3+} with different donor atoms. This finding is also surprising due to the high *kinetic lability* of Ni^{2+} cations and fast ligand exchange reactions in the coordination sphere [67]. Rate constants for water, methanol, ammonia, acetonitrile and DMF exchange in octahedral complexes of $[Ni(solv)_6]^{2+}$ are 3.2×10^4, 1.0×10^3, 7.0×10^4, 3.1×10^3 and $3.8 \times 10^3\,s^{-1}$, respectively [68]. This is seven to eight orders of magnitude faster than the rate of the solvent exchange in kinetically inert Cr^{3+} and Co^{3+} complexes. *Mer*- and *fac*-isomers are common in numerous hexacoordinate compounds [66]. The *fac*-$Ni(ACO)_3^-$ unit has a trigonal twist angle of ~20° between two parallel planes of nitrogen and oxygen atoms in the trigonal-prism (Fig. 2), because the angle between planes in an octahedral complex is 60°; the observed angle between O8b, O8, O8d and N2b, N2, N2d planes in **4** is ~40°.

All six cyanoxime anions in complex **4** are planar and demonstrate the *cis*-*anti* configuration contrary to that found in $MH(ACO)_2$ ($M = Na^+$, K^+) [55,56], $M'(ACO)$ ($M' = Rb^+$, Cs^+) [57], and several tellurium [69], antimony [16,19,70], and tin [26,71,72] compounds. In the latter three groups of compounds, the ACO^- ligands are bound to the Te(IV), Sb(IV) and Sn(IV) central atoms in a monodentate fashion via the oxygen of the oxime group. At the same time, the ACO^- anion exists in the



SCHEME 3

nitroso form in complex **4** and several other transition metal compounds. Thus, the N2–O3 bond length reported in complex **4** is 1.301(2) Å, and is shorter than the N2–C4 bond length, 1.313(4) Å (Table II). The C4–C7 bond length is 1.474(5) Å, close to a single bond and permits rotation of functional groups around the bond. This helps the cyanoxime adjust its conformation to the most favorable binding mode to a particular metal center (Scheme 3). The C7–N9 (1.323(5)) and C7–O8 (1.247(4) Å) bond lengths are shorter and longer than single and double bonds respectively, typical for amides (Table II).

Complex **4** cannot be obtained by direct reaction between Ni^{2+} and ACO^- anions in solution because of the fast formation of the insoluble red-purple $Ni(ACO)_2 \cdot 2Solv$ (Solv = H_2O, acetone or MeOH) [16,38,56].

There are also several known examples of Ni(II) and Cu(II) complexes [73–75] formed with the ACO^- ligands in highly basic conditions in which a second deprotonation of the anion at the amide nitrogen atom takes place. The resulting dianion coordinates to the copper and nickel ions via two nitrogen atoms [73–75] and retains the *trans-anti* configuration usually observed in HACO, its ionic salts such as M(ACO) and $MH(ACO)_2$ mentioned above, as well as organometallic Sb, Te and Sn derivatives.

CONCLUSION

The unique trimetallic anion in complex **4** was formed by demetallation of a diperchlorate Ni(II) complex containing the *meso*-{14ane[N_4]} macrocyclic ligand.

Complex **4** contains two *tris*-(cyanoximato(nickel(II)) anions combined into a trimetallic $[NaNi_2L_6]^-$ assembly by a central Na^+ cation. Individual $[Ni(ACO)_3]^-$ anions have a *fac* geometry and contain planar cyanoxime anions which adopt a *cis-anti* configuration and are in the *nitroso* form. This trimetallic $[NaNi_2L_6]^-$ complex cannot be obtained by direct reaction between Ni(II) and the amide-cyanoxime anions ACO^-.

The interaction between macrocyclic metallocomplexes and cyanoxime can be used as an alternative and much safer way for demetallation of transition metal-based macrocyclic compounds. Thus, sodium cyanide in such reactions may be effectively substituted for non-toxic NaL (L = cyanoxime anions [18,19]).

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Supplementary Material

Pages of Supplementary material: S1 for the synthesis of macrocyclic complexes and ligand **A**; S2 and S3 – proton and ^{13}C NMR spectra for the macrocycle **A**; S4 – table of atomic coordinates for the structure of complex **4**. Data deposited as *Electronic Supplementary Information* may be accessed free of charge via the Internet. Additional X-ray crystallographic data for complex **4** have been deposited with the Cambridge Crystallographic Data Center.

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