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Studies on Complexes of Metal(II) Carboxylates with Donor Molecules. IV.[1] Complexes of Nickel(II) Chloroacetates with Pyridine *N*-Oxides and Triphenylphosphine Oxide

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Synopsis. Twelve green crystalline complexes with the general formula $[Ni(O_2CR)_2 \cdot L]_2$ were prepared by the reaction of stoichiometric amounts of pyridine *N*-oxide, 2-methylpyridine *N*-oxide, 3-methylpyridine *N*-oxide, and triphenylphosphine oxide with nickel(II) mono-, di-, and trichloroacetates in methanol. The complexes were characterized by elemental analyses, conductance, magnetic moments, IR and electronic spectra as neutral, binuclear, carboxylato bridged species identical to those of copper(II) acetate monohydrate. The complexes involve varying degrees of magnetic interaction which diminishes with increasing chlorine substitution in the chloroacetate moiety.

Studies on binuclear metal(II) carboxylate complexes of the type $[M(O_2CR)_2 \cdot L]_2$ (especially, when M=Cu) reveal that the extent of magnetic interaction in these systems is largely determined by the nature of the carboxylate anion and the addend ligand.[2–4] However, in complexes of nickel(II) propionate and butyrate with aromatic amine oxides, we found that the magnetic moments of these complexes are independent of the nature of the alkanoate anion.[5] Since chloroacetic acids widely differ in acid strength, their nickel(II) complexes have been examined in order to assess the effect of varying basicity of the carboxylate anions on magnetic and other properties of the resulting complexes. The results of these studies are presented in this paper.

Experimental

Materials. Trinickel(II) carbonate tetrahydroxide tetrahydrate was repeatedly washed with hot water and then dried in the air. The chloroacetic acids and the amine oxide ligands were purified by vacuum distillation. Triphenylphosphine oxide hemihydrate was heated at 105 °C in a vacuum for 3 h and subsequently recrystallized from dry acetone to give the anhydrous compound (mp 154—155 °C). Nickel(II) chloroacetates were prepared as hydrates by the method of Lever and Ogden[6] and its modifications. The anhydrous samples obtained after drying in a vacuum over phosphorus pentaoxide gave satisfactory results in elemental analyses.

Complexes. The complexes were prepared by the direct interaction of the appropriate nickel(II) chloroacetate and the ligand in methanol, using the same general technique as given in the following example.

Bis(chloroacetato)(pyridine N*-oxide)nickel(II).* To a solution containing 1.48 g (6 mmol) nickel(II) chloroacetate in methanol (125 cm^3) was added, with stirring, a solution of 0.93 g (6.5 mmol) of freshly purified pyridine *N*-oxide in methanol (10 cm^3). The resulting green solution was concentrated to *ca.* 30 cm^3 and filtered while hot. Anhydrous diethyl ether (30 cm^3) was added to the cold filtrate and the green solid which separated out on allowing the filtrate to stand overnight was recrystallized from a 2:1 ethyl acetate–benzene mixture (60 cm^3) containing a small amount of pyridine *N*-oxide (0.15 g). The crystalline product was collected, washed with a 2:1 ethyl acetate–benzene mixture and then dried in a vacuum over phosphorus pentaoxide to yield 1.38 g (68% based on nickel(II) chloroacetate) of the required product.

The remaining nickel(II) chloroacetate complexes were prepared similarly in 50—80% yields. Reactions were also carried out using ligands in higher molar ratio of 1:2, 1:3, and a large excess but the products obtained were invariably of 1:1 stoichiometry, identical to those obtained with reactants in equimolar ratio.

Analyses. Nickel was determined gravimetrically as bis(dimethylglyoximato)nickel(II). Carbon and hydrogen analyses were carried out in the departmental microanalytical laboratory. For chlorine analysis, a sample containing 20—25 mg of chlorine was fused with a mixture of anhydrous sodium carbonate (0.5 g), sodium hydroxide (0.25 g) and sodium (0.1 g) at 700—900 °C for *ca.* 30 min in a platinum crucible. The resulting mass was extracted with distilled water, and the chloride contents of the alkaline extract were determined gravimetrically as silver chloride.

Measurements. Magnetic measurements were carried out at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. The electronic spectra were recorded in acetone over 8000—28500 cm^{-1} on a Beckman DK-2A spectrophotometer, while the infrared spectra were scanned on Perkin-Elmer 337 and 621 instruments as Nujol mulls in sodium chloride and polyethylene plates.

Results and Discussion

The results of elemental analyses indicate that the complexes are of 1:1 stoichiometry and can be formulated as $[Ni(O_2CR)_2 \cdot L]$. The complexes are light green to green in color. They are moderately soluble in polar solvents, but are generally insoluble in nonpolar solvents. Molar conductance values of the millimolar solutions of the complexes in methanol are of the order 20-40 S cm^2 mol^{-1} suggesting that the complexes are nonelectrolytic in nature. Molecular weights could not be determined by the cryoscopic method because of insufficient solubility of the complexes in benzene and nitrobenzene.

Electronic Spectra. The electronic spectra of the complexes show the usual three bands (I, III, and IV) around 9000, 15000, and 25000 cm^{-1} as observed in octahedral complexes of nickel(II); these bands are assigned to $^3T_{2g} \leftarrow {}^3A_{2g}$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$, and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ transitions.[7] An important feature of the electronic spectra of these complexes is that an additional band (II) is observed at $\approx$14000 cm^{-1}. The band is usually of lower intensity assigned to the spin forbidden, singlet transition $^1E_g(D) \leftarrow {}^3A_{2g}$, gaining intensity through configurational interaction or spin-orbit coupling.[7] The molar extinction coefficient values of the bands fall in the range 2.3—17 dm^3 cm^{-1} mol^{-1} similar to those reported for trans octahedral nickel(II) complexes.[6,7]

TABLE 1. ANALYSES, MAGNETIC MOMENTS, ELECTRONIC SPECTRA, AND IR-BANDS OF THE COMPLEXES

Complex	Found (Calcd) (%)				μ_{eff} a)	$\nu/10^3$ cm^{-1}				Important IR-band/cm^{-1}			
	C	H	Cl	Ni	B. M.	I	II	III	IV	$\nu_{NO \mid P=O}$	$\nu_{COO}(as)$	$\nu_{COO}(sy)$	$\Delta\nu_{COO}$
$[Ni(O_2CCH_2Cl)_2(C_5H_5NO)]_2$	32.05 (31.70)	3.05 (2.64)	20.36 (20.84)	17.15 (17.23)	2.64	9.0	13.9	15.2	24.6	1217	1630	1374	256
$[Ni(O_2CCH_2Cl)_2(2\text{-}CH_3C_5H_4NO)]_2$	— (33.83)	— (3.10)	19.11 (20.02)	16.38 (16.55)	—	8.9	14.0	15.1	24.8	1209	1622	1372	250
$[Ni(O_2CCH_2Cl)_2(3\text{-}CH_3C_5H_4NO)]_2$	33.60 (33.83)	3.55 (3.10)	19.87 (20.02)	16.56 (16.55)	2.63	9.0	13.7	15.2	25.1	1258	1634	1376	258
$[Ni(O_2CCH_2Cl)_2(C_6H_5)_3PO]_2$	49.90 (50.41)	4.05 (3.63)	13.11 (13.56)	11.02 (11.21)	2.79	8.9	13.7	15.0	24.9	1168	1638	1376	262
$[Ni(O_2CCHCl_2)_2(C_5H_5NO)]_2$	26.05 (26.36)	2.50 (1.71)	34.21 (34.66)	14.28 (14.33)	2.82	9.0	14.0	15.4	25.4	1222b) 1210	1645	1355	290
$[Ni(O_2CCHCl_2)_2(2\text{-}CH_3C_5H_4NO)]_2$	27.90 (28.32)	2.55 (2.12)	32.72 (33.51)	14.05 (13.86)	2.80	9.0	14.1	15.3	25.1	1208	1647	1355	292
$[Ni(O_2CCHCl_2)_2(3\text{-}CH_3C_5H_4NO)]_2$	28.20 (28.32)	2.55 (2.12)	32.96 (33.51)	13.72 (13.86)	2.80	9.0	13.7	15.3	25.1	1220	1651	1360	291
$[Ni(O_2CCHCl_2)_2(C_6H_5)_3PO]_2$	— (44.54)	— (2.81)	23.01 (23.96)	9.76 (9.91)	—	8.8	13.6	15.1	25.0	1168	1645	1350	295
$[Ni(O_2CCCl_3)_2(C_5H_5NO)]_2$	22.55 (22.56)	1.15 (2.04)	43.87 (44.49)	12.46 (12.26)	3.07	8.8	13.6	15.2	25.6	1218	1695	1346	349
$[Ni(O_2CCCl_3)_2(2\text{-}CH_3C_5H_4NO)]_2$	24.50 (24.35)	1.50 (1.42)	42.44 (43.23)	11.80 (11.92)	3.11	9.0	13.5	15.0	25.1	1220	1690	1345	345
$[Ni(O_2CCCl_3)_2(3\text{-}CH_3C_5H_4NO)]_2$	24.60 (24.35)	1.55 (1.42)	42.67 (43.23)	11.40 (11.92)	3.12	8.9	13.7	15.3	25.2	1257	1690	1344	346
$[Ni(O_2CCCl_3)_2(C_6H_5)_3PO]_2$	39.85 (39.90)	2.50 (2.27)	32.19 (31.67)	8.67 (8.87)	3.21	8.9	13.8	15.1	25.5	1170	1690	1340	350

a) At room temperature, 290 K. b) Shoulder.

Magnetic Properties. The magnetic moments of the complexes (Table 1) fall in the range 2.60—3.21 BM which are, in general, less than the magnetic moments of 3.15—3.30 BM observed for magnetically normal, octahedral nickel(II) carboxylate complexes.[8)] This suggests that the complexes involve some metal–metal interaction and may have a binuclear (or polynuclear), carboxylato bridged structure similar to some nickel(II) trihaloacetate complexes.[9)]

The magnetic moment values of the present complexes are significantly higher than the values of 2.35—2.63 BM observed for nickel(II) alkanoate complexes,[7)] showing a regular increase from mono-, to di- and trichloroacetate complexes. This indicates that the magnetic interaction in these complexes decreases sharply as the basicity of the chloroacetate anion decreases with increasing chlorine substitution in the acetate moiety.

Infrared Spectra. The N–O stretching frequency which occurs at 1250, 1244, and 1278 cm^{-1} in pyridine *N*-oxide, 2-methylpyridine *N*-oxide, and 3-methylpyridine *N*-oxide is shifted to lower frequencies by 20—60 cm^{-1} in the nickel(II) chloroacetate complexes. This indicates monodentate coordination of pyridine *N*-oxide ligands.[10)] δ_{N-O} and γ_{C-H} also show some positive or negative shifts confirming the coordination of *N*-oxide ligands through their oxygen atoms. The P=O stretching vibration shows a negative shift of 19—21 cm^{-1}, while $\delta_{P=O}$ and γ_{C-H} also undergo small shifts indicating that triphenylphosphine oxide is coordinated through its P=O oxygen atom in its complexes.[11)]

The asymmetric carboxyl stretching frequency in nickel(II) mono-, di-, and trichloroacetate complexes occurs as a very strong peak at 1638—1622, 1651—1645, and 1695—1690 cm^{-1}, while the symmetric carboxyl stretching frequency is observed at 1376—1372, 1360—1350, and 1346—1340 cm^{-1}, respectively. The upwards shift of $\nu_{COO}(as)$ and downward shift of $\nu_{COO}(sy)$ noted in these complexes is ascribed to the increasing chlorine substitution in the chloroacetate anion.[12)] The position and nature of the carboxyl stretching frequencies, as well as their separation, are comparable to the frequencies reported by Lever and Ogden for nickel(II) complexes containing bidentate bridging chloroacetato groups.[6)] All this corroborates the view that the complexes under investigation are binuclear, carboxylato bridged species identical to copper(II) acetate monohydrate.[13)]

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