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Preparation and Characterization of Isothiocyanatomanganese(III) Complexes of Tetraaza[14]annulenes

KAZUNORI SAKATA[‡], HIDEHIKO NAKAMURA and MAMORU HASHIMOTO

Department of Chemistry, Kyushu Institute of Technology, Tobata-ku, Kitakyushu 804, Japan

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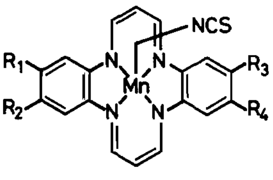
Although the chemistry of manganese–porphyrin complexes has been widely studied [1], examples of N_4-macrocyclic ligand complexes to manganese are rare. Dabrowiak *et al.* reported the synthesis and characterization of the manganese complex with the saturated N_4-macrocycle [2, 3]. We have investigated oxovanadium(IV), nickel(II), copper(II) and palladium(II) complexes of unsaturated N_4-macrocycles from the viewpoint of their spectral properties [4].

In the present work, we employed two manganese(III) complexes of unsaturated N_4-macrocycles; isothiocyanato(dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato manganese(III) (*1*) and isothiocyanato-(2,3,11,12-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)manganese(III) (*2*). We characterized the optical and magnetic properties of isothiocyanatomanganese(III) chelates of the present macrocycles by means of electronic and vibrational spectroscopy as well as by magnetic susceptibility measurements.



(1) $R_1=R_2=R_3=R_4=H$
(2) $R_1=R_2=R_3=R_4=CH_3$

Kosower studied the solvent effects on the charge-transfer (CT) transition for the 1-ethyl-4-methoxycarbonylpyridinium iodide complex in various solvents [5–7]. Murakami *et al.* made a systematic study of the solvent effects on CT transitions in which the Co–CN bond of the dicyano(8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinato)cobalt(III) is involved [8].

Since no systematic study of the solvent effects on CT transitions for manganese complexes has been carried out, we also report the solvent effects in the 520–560 nm region for isothiocyanato manganese(III) complexes.

Experimental

Preparation of Macrocycles

5,14-Dihydro-2,3,11,12-tetramethyldibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecine

After a 7.0 g sample of 2-propynal [9] dissolved in methanol (5 ml) was added dropwise with stirring for 1 h at 70–80 °C into a mixture of 1,2-diamino-4,5-dimethylbenzene (8.4 g), methanol (40 ml), and N,N-dimethylformamide (40 ml), the reaction mixture was refluxed for 1 h with stirring. Upon cooling the mixture with ice-water, the crystalline solid was recovered by filtration and recrystallized from N,N-dimethylformamide–methanol to give glittering dark red needles; yield 3.9 g (37%). IR (KBr disk): 3200 (N–H str.), 1630 (C=N str.), and 1550 cm^{-1} (macrocyclic skeletal str.). NMR ($CDCl_3$, TMS)*: δ 2.16 (12H, s, 2-CH_3, 3-CH_3, 11-CH_3, and 12-CH_3), 4.90 (2H, t, J = 6.5 Hz, =CH–C*H*=CH–), 6.79 (4H, s, aromatic), 7.58 (4H, t, J = 6.5 Hz, –N=C*H*–CH= and –CH=C*H*–NH–), and 13.8 ppm (2H, t, J = 6.5 Hz, –N*H*). *Anal.* Found: C, 76.64; H, 7.24; N, 16.05%; M^+, 344**. Calcd. for $C_{22}H_{24}N_4$: C, 76.71; H, 7.02; N, 16.27%; M, 344.46.

The synthesis procedure for 5,14-dihydrodibenzo-[b,i][1,4,8,11]tetraazacyclotetradecine has been described previously [4].

Preparation of Complexes

Isothiocyanato(dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)manganese(III) (1)

A mixture of 5,14-dihydrodibenzo[b,i][1,4,8,11]-tetraazacyclotetradecine (0.20 g), manganese(II) acetate tetrahydrate (0.20 g), and N,N-dimethylformamide (80 ml) was heated under reflux for 45 min. To the hot mixture, water was added (250 ml), and the reaction mixture was filtered. After addition of potassium thiocyanate (1.0 g), the mixture was allowed to stand in a refrigerator for 3 h. The crystalline solid was recovered by filtration, washed with methanol, and recrystallized from N,N-dimethylformamide as glittering dark violet plates; yield 0.22 g (79%). *Anal.* Found: C, 57.77; H, 3.55; N, 17.23%; M^+, 399**. Calcd. for $C_{19}H_{14}N_5SMn$: C, 57.14; H, 3.53; N, 17.54%; M, 399.35.

[‡] Author to whom correspondence should be addressed.

*NMR spectrum was taken on a JEOL JNM-FX 60 spectrometer.

**Mass spectral measurements were carried out with a JEOL JMS-DX 300 gas chromatograph-mass spectrometer.

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TABLE I. Magnetic Susceptibility Results for Macrocyclic Manganese(III) Complexes.

Complex[a]	Coordination number	No. of unpaired electrons	μ_{eff} B.M.	$[4S(S+1)]^{1/2}$	Temp. (K)	Ref.
(*1*)	5	4	4.91	4.90	296.0	This work
(*2*)	5	4	4.89	4.90	296.0	This work
Mn(III)Hemato-IX-Cl	5	4	4.88	4.90	77–300	10

[a] (*1*), Isothiocyanato(dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)manganese(III); (*2*), isothiocyanato(2,3,11,12-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)manganese(III); Hemato-IX, 2,7,12,18-tetramethyl-3,8-di(1-hydroxyethyl)-13,17-dicarboxyethylporphine.

Isothiocyanato(2,3,11,12-tetramethyldibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecinato)manganese(III) (*2*) was obtained in a manner similar to that described above for manganese(III) complex (*1*) and recrystallized from 2-methoxyethanol, giving dark violet plates; yield 78%. *Anal.* Found: C, 60.01; H, 4.85; N, 15.13%; M^+, 455**. Calcd. for $C_{23}H_{22}N_5SMn$: C, 60.65; H, 4.87; N, 15.38%; M, 455.46.

Physical Measurements

Magnetic susceptibility measurements of solid powdered samples were carried out by the Faraday method. Calibrations were made with the aid of $Ni(en)_3S_2O_3$***, while diamagnetic corrections were performed by using Pascal's constants. Infrared spectra in the range of 650–4000 cm^{-1} were measured with a JASCO IRA-2 grating spectrophotometer at room temperature using a KBr disk method. Electronic spectra covering the 16000–32000 cm^{-1} range were recorded on a Shimadzu UV-200S double beam spectrophotometer at room temperature.

Results and Discussion

The results of magnetic susceptibility measurements are summarized in Table I together with that for Mn(III)Hemato-IX-Cl [10]. It became apparent that the manganese(III) complexes (*1,2*) contain a high-spin system. The effective magnetic moments indicate that the nuclear manganese has an oxidation state of +3, which is consistent with the spin-only value and that found for Mn(III)Hemato-IX-Cl.

In the ordinary infrared region, the (*1*) and (*2*) complexes give an intense absorption band at *ca.* 2050 cm^{-1} which is associated with the C≡N stretching mode of the SCN^- anion. The C≡N stretching bands for (*1*) and (*2*) complexes are listed in Table II along with the comparable data for Fe(OEP)NCS [11], $(NEt_4)_2[Co(NCS)_4]$, and $K[Au(SCN)_4]$ [12]. The SCN group may coordinate to a manganese through the nitrogen or the sulfur. The C≡N stretching frequencies are generally lower in N-bonded complexes (near and below 2050 cm^{-1}) than in S-bonded complexes (near 2100 cm^{-1}) [13]. Several researchers considered the C–S stretching mode as a structural diagnosis: 860–780 cm^{-1} for N-bonded, and 720–690 cm^{-1} for S-bonded, complexes [14]. The latter has not been shown to be diagnostic of N or S bonded SCN group, because the C–S stretching mode in this work is apparently obscured by ligand absorptions. The (*1*) and (*2*) complexes are N-bonded as judged by the C≡N stretching frequency.

TABLE II. Vibrational Frequencies of Isothiocyanato and Thiocyanato Complexes (cm^{-1}).

Complex[a]	ν(C≡N)	Type	Ref.
(*1*)	2048	N-bonded	This work
(*2*)	2050	N-bonded	This work
Fe(OEP)NCS	2042	N-bonded	11
$(NEt_4)_2[Co(NCS)_4]$	2062	N-bonded	12
$K[Au(SCN)_4]$	2130	S-bonded	12

[a] See Table I for numbering the manganese complexes (*1*) and (*2*); OEP, 2,3,7,8,12,13,17,18-octaethylporphine; NEt_4, tetraethylammonium.

Visible and ultraviolet spectra covering the 16000–32000 cm^{-1} region are shown in Fig. 1 for (*1*) and (*2*) complexes. The absorption bands observed in the 18000–29000 cm^{-1} region are reasonably attributed to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and CT transitions from metal to ligand, and not of $d \rightarrow d^*$ origin as in the case of $[Mn(III)[14]aneN_4X_2]^{+}$§ [2]. Two reasons for this conclusion are

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***en, ethylenediamine.

§ $[14]aneN_4$, meso-5,7,7,12,14,14-hexamethyl[1,4,8,11]-tetraazacyclotetradecane.

TABLE III. Solvent Effects on CT-Bands for Isothiocyanatomanganese(III) Complexes.

Complex		(*1*)[a]		(*2*)[a]	
Solvent	Z-value[b]	λ_{max} (nm)	E_T[c] (kcal mol^{-1})	λ_{max} (nm)	E_T[c] (kcal mol^{-1})
C_6H_6	54.0	555	51.5	559	51.1
C_6H_5Cl	58.0	551	51.9	558	51.2
$CH_3CO_2C_2H_5$	59.4	546	52.4	553	51.7
o-$C_6H_4Cl_2$	60.0	550	52.0	555	51.5
$CHCl_3$	63.2	546	52.4	554	51.6
CH_2ClCH_2Cl	63.9	544	52.6	555	51.5
CH_2Cl_2	64.2	542	52.7	551	51.9
$(CH_3)_2CO$	65.7	540	52.9	550	52.0
CH_3CN	71.3	534	53.5	546	52.4
CH_3COOH	79.2	528	54.1	540	52.9

[a] See Table I for numbering manganese complexes (*1*) and (*2*). [b] Cited from ref. [5]. [c] Calculated from E_T (kcal mol^{-1}) = $2.859 \times 10^5/\lambda_{max}$ (in Å).

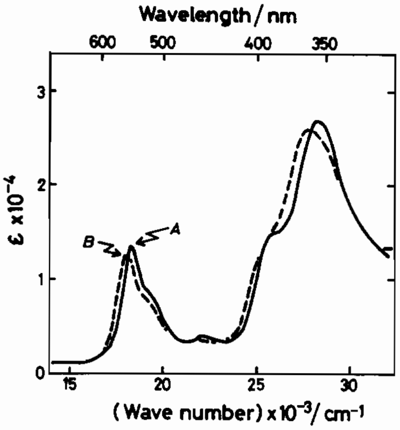

Fig. 1. Electronic absorption spectra of isothiocyanatomanganese(III) complexes in 1,2-dichloroethane at room temperature. *A*: (*1*), *B*: (*2*).

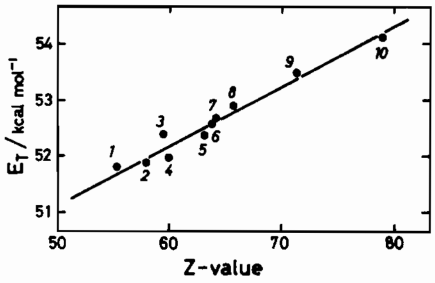

Fig. 2. Correlation between CT transition energy of manganese(III) chelate (*1*) and solvent polarity parameter (Z): *1*, benzene; *2*, chlorobenzene; *3*, ethyl acetate; *4*, 1,2-dichlorobenzene; *5*, chloroform; *6*, 1,2-dichloroethane; *7*, dichloromethane; *8*, acetone; *9*, acetonitrile; *10*, acetic acid.

as follows. The molar extinction coefficients of the bands (~10^4 mol^{-1} cm^{-1} l) are larger than those usually assigned to d → d* transitions [15]. In addition, the general feature of the spectra for (*1*) and (*2*) complexes is similar to those observed for the dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinatometal complexes which have been reported previously [4].

An intense absorption band in the 528–559 nm region is ascribed to the intramolecular CT transition for which the Mn–NCS bond is interrelated. The reason for this assignment is given below. The transition energy (E_T) is moderately sensitive to the solvent character as may be seen in Table III. The behavior of the manganese chelates examined here is analogous to that obtained for dicyano(8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinato)cobalt(III) reported by Murakami *et al.* [8]. Although no linear relationship between E_T-values and D-values (the solvent dielectric constant), there exists a linear relationship between E_T-values and Z-values as shown in Fig. 2.

The Z-value was defined, as an empirical measure of solvent polarity based on the CT band of 1-ethyl-4-methoxycarbonylpyridinium iodide complex in various solvents, by Kosower [5–7]. The position of the CT band of the pyridinium iodide complex measures the extent of interaction of a dipole with a cybotactic region of a solvent. Accordingly, the present absorption band is assigned to the so-called intramolecular CT transition.

In conclusion, the manganese complexes (*1, 2*) have the N_5-penta-coordination structure in the trivalent state of the nuclear metal and maintain a spin-free d^4 ($S = 2$) state. Judging from the C≡N stretching frequency in the infrared region, the SCN group coordinates the manganese through the nitrogen. An intense absorption band in the 528–559 nm range is assigned to the intramolecular CT transition associated with the Mn–NCS bond.

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