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Some TCNQ Simple and Complex Salts of Nickel and Copper Macrocyclic Complexes*

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Abstract

Fourteen new TCNQ (7,7,8,8-tetracyanoquinodimethane) simple salts of the type $ML(TCNQ)_2$ and complex salts of the type $ML(TCNQ)_3$, where M = nickel or copper and L = macrocyclic ligands, have been synthesized. The IR spectra of all the complex salts showed a strong absorption band at about 2300–4000 cm^{-1} indicating the charge transfer between $TCNQ^0$ and $TCNQ^-$. The interaction between $TCNQ^-$ caused the activation of TCNQ IR non-active A_g vibrations demonstrating the charge transfer between $TCNQ^-$ species. The electronic absorption spectra gave two strong absorption bands at about 16.5×10^3 and 26.5×10^3 cm^{-1} caused by the local excitation in $TCNQ^0$ or $TCNQ^-$. The ESR spectra did not show a clear interaction between the copper ions. Based on these facts one could imagine segregated stacks of the metal complex cations and of $TCNQ^-$ anions. This one-dimensional structure of $TCNQ^-$ resulted in a good conductivity in the order of $\sigma_{RT} = 10^{-1}$–10^{-4} ohm^{-1} cm^{-1} for some of these complex salts.

Introduction

A series of TCNQ salts of transition-metal complexes have been prepared [1]. The observed conductivities are given in parentheses: $Cu(NH_3)_2(TCNQ)_2$ (1.4×10^{-3}); $Cu(en)_2(TCNQ)_2$ (2.5×10^{-5}) (en = $H_2NCH_2CH_2NH_2$); Cu(2,2′-dipyridylamine)$(TCNQ)_2$ (2.5×10^{-2}); M(1,10-phenanthroline)$_3$ $(TCNQ)_2 \cdot 6H_2O$ (M = Fe, 10^{-6}; M = Ni, 10^{-8}); Ni(1,10-phenanthroline)$_2(TCNQ)_2 \cdot 6H_2O$ (5×10^{-9}); $Cr_2(acetate)_4(OH)(TCNQ) \cdot 6H_2O$ (10^{-9} ohm^{-1} cm^{-1}).

It was found [2–5] that the high conductivity was associated with a crystal structure in which planar molecules were packed fáce-to-face with segregated stacks of metal cations and TCNQs. The π-overlap and charge transfer between adjacent molecules in the stacking direction caused the unpaired electrons to be partially delocalized along these one-dimensional molecular stacks and enabled them to conduct in that direction.

Recently some TCNQ salts of planar nickel complexes with macrocyclic ligands: Ni(TMP)(TCNQ) (TMP = tetramethylporphyrinato) [6] and Ni(DADMTA)(TCNQ) (DADMTA = 3,6-diacetyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene) [7] have been reported. Both salts consisted of mixed stacks bearing medium conductivities of 10^{-5} and 10^{-4} ohm^{-1} cm^{-1}.

In this paper we report the preparation and properties of some new TCNQ salts from nickel and copper complexes with various macrocyclic ligands.

Experimental

Syntheses

The tetraaza macrocyclic ligands complexing with the nickel and copper cations were 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (HMTADE), *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (HMTA), 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene (DMTADE), 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (TMTATE), 2,4,4,9,-11,11-hexamethyl-1,5,8,12-tetraazacyclotetradeca-1,5,8,12-tetraene (HMTATE), 1,4,7,10-tetraazacyclododecane (TACD), and 1,4,7,10-tetraazacyclotridecane (TACT).

These ligands and the corresponding metal complexes were prepared according to literature methods [8–15].

The simple salts were prepared by the reaction of $ML(ClO_4)_2$ or $MLCl_2$ with LiTCNQ in hot H_2O–

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CH_3CN. The complex salts were obtained from the reaction of LiTCNQ, TCNQ in CH_3OH–CH_3CN and $ML(ClO_4)_2$ in H_2O–CH_3CN. Fourteen simple and complex salts were obtained: Ni(HMTADE)(TCNQ)$_3$ (**1**), Cu(HMTADE)(TCNQ)$_3$ (**2**), Ni(HMTA)(TCNQ)$_2$ (**3**), Ni(HMTA)(TCNQ)$_3$ (**4**), Cu(HMTA)(TCNQ)$_2$ (**5**), Ni(TMTATE)(TCNQ)$_3$ (**6**), Cu(TMTATE)(TCNQ)$_3$ (**7**), Ni(en)$_2$(TCNQ)$_2$ (**8**), Ni(en)$_2$(TCNQ)$_3$ (**9**), Ni(HMTATE)(TCNQ)$_3$ (**10**), Ni(TACD)(TCNQ)$_3$ (**11**), Cu(TACT)(TCNQ)$_3$ (**12**), Cu(DMTADE)(TCNQ)$_3$ (**13**), and Cu(DMTADE)(TCNQ)$_2$ (**14**). All these salts were characterized by elemental analysis and IR, some of them by electronic absorption spectroscopy and ESR. The conductivities of some salts were measured.

Measurements

Elemental analyses were performed at the Analytical Laboratory, Institute of Elementoorganic Chemistry (see 'Supplementary Material'). IR spectra were recorded on a Nicolet FT-IR 5DX spectrometer. Electronic absorption spectra were obtained for solid samples by reflection measurement on a Shimadzu UV-365 spectrometer. ESR spectroscopy was studied on a JES-FEIXG ESR spectrometer. The conductivities were measured on an England 35-7075 galvanometer at room and variable temperatures.

Results and Discussion

IR Spectra

The IR data are given in Table I.

The IR spectra of all complex salts show broad strong absorption bands at about 4000–2300 cm^{-1} characteristic for the electron transfer between $TCNQ^0$ and $TCNQ^-$ [1a]. The CN group absorption for neutral TCNQ appears at 2224 cm^{-1} as a sharp singlet, but the IR spectra of all salts exhibit two or three bands in the CN stretching region, 2193–2155 cm^{-1}, indicating the existence of $TCNQ^-$ A_g and B_u modes, as well as the B_u mode of $TCNQ^0$ [16]. The activation of other TCNQ IR non-active A_g modes can also be seen: at about 1580 cm^{-1} (A_g-3, ring and external C=C and C–C stretching and CCH bending), about 1330–1340 cm^{-1} (A_g-4, ring and external C=C stretching), and about 1170–1180 cm^{-1} (A_g-5, CCH bending). The activation of the A_g modes is specific only in a $TCNQ^-$ system having intermolecular interactions [17, 18]. From the above IR data one could imagine the presence of $(TCNQ)_2^{2-}$ or $(TCNQ)_3^{2-}$ units and the aggregation of these to a one-dimensional stack.

Electronic Absorption Spectra

The spectra measured for solid state salts **1**–**9** show two strong absorption bands at about 16.5×10^3 and 26.5×10^3 cm^{-1}. These bands should be

TABLE I. Infrared Spectral Data (cm^{-1})^a

1	Ni(HMTADE)TQ$_3$	>2300(s,b), 2190(s), 2180(s), 2165(s), 1655(w), 1581(m), 1507(m), 1343(s), 1179(m), 1056(w,b), 834(w), 826(w), 671(s)
2	Cu(HMTADE)TQ$_3$	>2300(s,b), 2188(s,b), 2155(s,b), 1655(m), 1573(s), 1507(m), 1352(s), 1330(s), 1171(s), 1056(w), 982(w), 958(w), 835(w), 826(w), 704(s), 671(m)
3	Ni(HMTA)TQ$_2$	3140(m), 2183(s), 2158(m), 1582(m,sp), 1505(m,sp), 1347(m), 1181(m,sp), 982(w), 830(w), 719(w)
4	Ni(HMTA)TQ$_3$	>2300(s,b), 2191(s), 2177(s), 1574(m), 1521(w), 1505(w), 1365(m), 1351(m), 1171(m), 1151(m,sh), 982(w), 958(w), 835(w), 828(w), 703(m)
5	Cu(HMTA)TQ$_2$	3180(m), 2183(s), 2159(s), 1583(m,sp), 1504(m,sp), 1362(m), 1341(m), 1176(s,sp), 982(w), 829(w), 721(w)
6	Ni(TMTATE)TQ$_3$	>2300(s,b), 2192(s), 2184(s), 2163(s), 1576(m), 1504(m), 1370(w), 1347(s), 1178(m), 980(w), 837(w), 703(w)
7	Cu(TMTATE)TQ$_3$	>2300(s,b), 2190(s), 2177(s), 2158(s), 1575(m), 1570(m), 1506(m), 1340(m), 1332(m), 1171(m,b), 1153(m), 957(w), 834(w), 703(w)
8	Ni(en)$_2$TQ$_2$	3353(w), 3287(w), 2190(s), 2176(s), 2154(s), 1574(s), 1506(m), 1496(m), 1392(w), 1328(s), 1173(s), 1007(m), 832(w), 710(w), 668(w)
9	Ni(en)$_2$TQ$_3$	>2300(s,b), 2192(s), 2188(s), 2156(s), 1581(s), 1499(m), 1395(w), 1343(m), 1179(m), 1007(w), 834(w), 826(w), 671(m)
10	Ni(HMTATE)TQ$_3$	>2500(s,b), 2191(s), 2180(s), 2161(s), 1643(w), 1581(m), 1533(w), 1507(m), 1353(m), 1320(w), 1182(w), 1072(w), 860(w), 827(w), 701(w)
11	Ni(TACD)TQ$_3$	>2300(s,b), 2191(s), 2160(s,b), 1574(m), 1504(m), 1344(s), 1321(m), 1169(m), 1086(m), 1133(m), 987(w), 945(w), 700(m)
12	Cu(TACT)TQ$_3$	>2300(s,b), 2193(s), 2185(s), 2161(s), 1578(m), 1561(m), 1507(m), 1367(m,b), 1178(m), 1099(w), 990(w), 959(w), 705(w)
13	Cu(DMTADE)TQ$_3$	>2300(s,b), 2193(s), 2175(s), 1577(m), 1539(w), 1507(m), 1396(w), 1368(m), 1343(m),

(continued)

TABLE I. *(continued)*

		1179(m), 1100(w), 1068(w), 985(w), 824(w), 718(w)
14	Cu(DMTADE)TQ$_2$	3152(w), 3125(w), 2190(s), 2163(s), 1579(m), 1539(w), 1505(m), 1388(w), 1349(m), 1179(m), 984(w), 863(w), 827(w), 719(w)
	TCNQ	3051(s,sp), 2224(s,sp), 1353(m, sp), 1124(w), 862(s,sp), 475(s)

[a]TQ = TCNQ, s = strong, m = medium, w = weak, b = broad, sp = sharp, sh = shoulder.

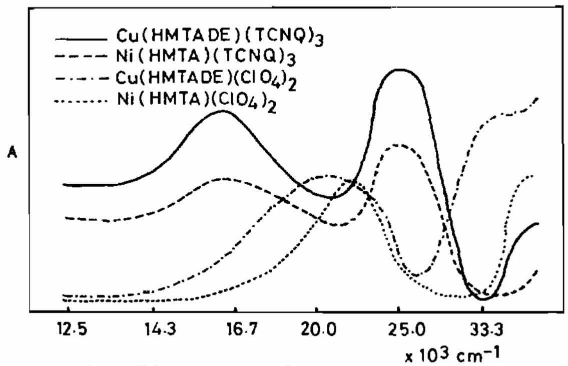

Fig. 1. The solid state absorption spectra.

assigned to local excitation (LE) bands of TCNQ^0 or TCNQ$^-$ [19, 20]. Figure 1 shows the spectra for salts **2** and **4** and the corresponding ML(ClO$_4$)$_2$ complexes. One can see also the disappearance of the characteristic absorptions for square planar Cu^{2+} d–d transition at 20 X 10^3 cm^{-1} and that for Ni^{2+} at 23 X 10^3 cm^{-1} [21].

Electrical Measurements

The conductivities (in ohm^{-1} cm^{-1}) of pressed pellets were measured by the four-electrode method for salts **1**, **2**, **3**, **4**, **8**, and **9** at room and variable temperatures. The room temperature conductivities and the electrochemical activation energies (in eV) obtained from the equation $\sigma = \sigma_0 \exp(-E/kT)$ are listed in Table II and the plots of lg σ *versus* $1/T$ for salts **2** and **4** are given in Fig. 2.

TABLE II. Conductivities and Electrochemical Activation Energies of TCNQ Salts

Salt		σ_{RT} (ohm^{-1} cm^{-1})	E_a (eV)
1	Ni(HMTADE)TQ$_3$ [a]	0.16	0.18
2	Cu(HMTADE)TQ$_3$	0.02	0.10
3	Ni(HMTA)TQ$_2$	1 x 10^{-7}	
4	Ni(HMTA)TQ$_3$	0.007	0.11
8	Ni(en)$_2$TQ$_2$	8 x 10^{-5}	
9	Ni(en)$_2$TQ$_3$	5 x 10^{-4}	

[a]TQ = TCNQ.

The conductivities for all salts measured are in the range of a typical semiconductor, but values for the complex salts **1**, **2**, **4** and **9** are higher (correspondingly lower activation energies) than for the simple salts **3** and **8**. The plots in Fig. 2 show satisfactory linear relationships between lg σ and $1/T$. Salt **2** has a transition temperature at 265 K and the activation energy changes from 0.10 to 0.33 eV. Accordingly, salt **4** has a transition temperature at 244 K and the activation energy changes from 0.11 to 0.14 eV.

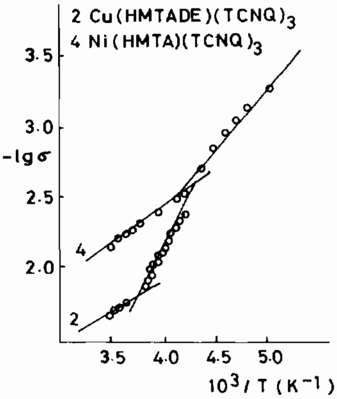

Fig. 2. Temperature dependence of the d.c. electrical conductivity of TCNQ salts.

ESR Spectra

The ESR spectra of CuL(ClO$_4$)$_2$ (L = HMTADE, HMTA and TMTATE) at room temperature are similar and give an unsymmetrical singlet indicating the spin–spin relaxation between Cu^{2+}. The ESR spectra of corresponding salts **2**, **5**, and **7** clearly show the anisotropy in g value and fine-structural splitting. The ESR spectra of Cu(HMTADE)(ClO$_4$)$_2$ and the simple salt **5** are shown in Fig. 3. From Fig. 3b two parallel signals can be seen, another two in high field are sheltered. The calculated $g_\parallel = 2.183$, $A_\parallel = 20.4 \times 10^{-3}$ cm^{-1}; $g_\perp = 2.050$, $A_\perp = 2.1 \times 10^{-3}$ cm^{-1} which means the disappearance of spin–spin relaxation between Cu^{2+}, *i.e.* CuL^{2+} species in salt **5** are not in face-to-face stacking. So, the structure of the TCNQ salts studied in this work may be similar to that of Pt(bipy)$_2$(TCNQ)$_3$ [22] having a regular stack of TCNQ species and irregular arrangement of metal cations around the TCNQ stack. The one-dimensional construction of TCNQ delocalized π orbital dominates the high conductivity while the metal cations make little contribution.

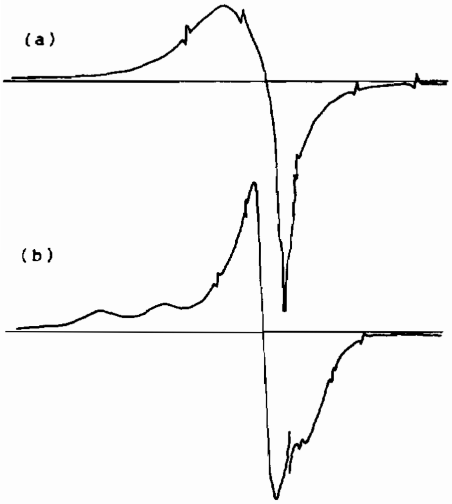

Fig. 3. ESR spectra observed for (a) Cu(HMTADE)$(ClO_4)_2$ and (b) Cu(HMTA)$(TCNQ)_2$ at ambient temperature.

Supplementary Material

Elemental analyses tables are available from the authors on request.

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