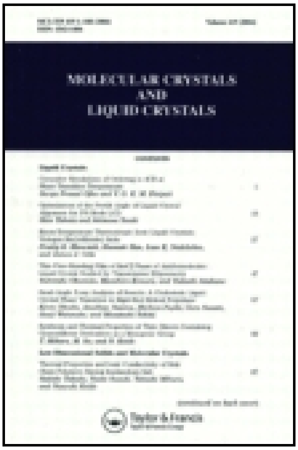

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# Synthesis and Electrical Resistivities of Transition-Metal Cation-TCNQ-Cyclam Complexes

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# SYNTHESIS AND ELECTRICAL RESISTIVITIES OF TRANSITION-METAL CATION-TCNQ-CYCLAM COMPLEXES

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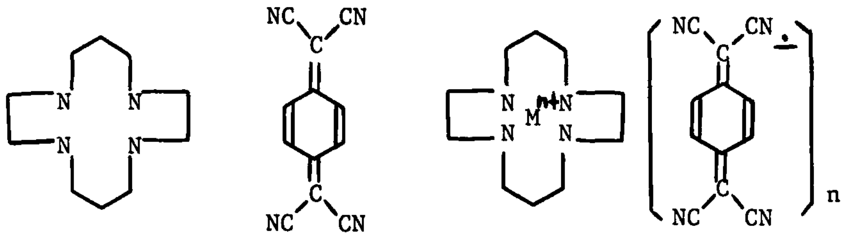
The complexes of 1,5,8,12-tetraazacyclotetradecane with transition-metal cation-TCNQ salts were synthesized. Their electrical resistivities were measured with the compacted samples at room temperature. They were found to be semiconductors with the resistivities of 31 to $1.0 \times 10^7$ Ωcm.

## INTRODUCTION

We have synthesized many cation-TCNQ-crown ether complexes.[1,2,3] Cations we used are alkali-metal ions, alkaline-earth metal ions, alkyl- and aryl-ammonium ions, and rare-earth ions. Alkaline-earth metal comlexes were much more conductive than alkali-metal complexes. These facts were explained by the closer distance between the TCNQ molecules for the former complexes than for the latter ones. Thus, transition-metal-TCNQ crown ether complexes are expected to be highly conductive. However, crown ethers do not include transition-metal ions so strongly as alkali-metal and alkaline-earth metal ions. Instead of crown ethers, we used 1,5,8,12-tetraazacyclotetradecane (usually called cyclam), which is known to include transion-metal ions strongly, and synthesized transition-metal-cation-TCNQ-cyclam complexes in expectation of highly conductive materials.

## SYNTHESIS OF TRANSITION-METAL-CATION-TCNQ-CYCLAM COMPLEXES

Cyclam was synthesized according as the reported procedures.[4] Transition-metal-cation-TCNQ-cyclam complexes were synthesized




cyclam TCNQ cation-TCNQ-cyclam complex

as follows. Cyclam-inorganic salts were first synthesized. The cyclam complexes with Ni, Cu, Zn, Rh, Co, La, Mn, and Pd ions were obtained by the reported procedure.[5,6] The following inorganic salts were used: $Ni(ClO_4)_2$, $Cu(ClO_4)_2 6H_2O$, $Zn(ClO_4)_2$, $RhCl_3 3H_2O$, $CoCl_2 6H_2O$, $La(NO_3)_3 6H_2O$, $Mn(ClO_4)_2 6H_2O$, and $PdCl_2$. The cyclam-inorganic salts thus obtained were reacted with Li TCNQ in the next step. This step is subdivided into two: (1) the cyclam-inorganic salt (Ni or Cu salt) was dissolved into acetonitrile, and an ethanol solution of Li TCNQ (equimolar amount) was added from a dropping funnel at room temperature. The precipitate was collected, washed with ethanol, and dried in vacuum; (2) cyclam-inorganic salt (Zn, Rh, Co, La, Mn, or Pd salt) was dissolved into water, and aqueous solution of Li TCNQ (1.1 molar ratio) was added from a dropping funnel. The precipitate was collected, washed with a large amount of water, and dried in vacuum.

Table 1 summarizes the complexes isolated,[7] their yields, and analytical data. The complexes having La, Mn, and Pd ions have respectively four, six, and four TCNQ molecules, judging from the analytical data. Figure 1 shows the diffuse reflection spectra of these three complexes. The absorption bands at the lower wavenumber than $10 \times 10^3$ $cm^{-1}$ measured in these complexes correspond to the charge-transfer transition from TCNQ anion radical to neutral TCNQ.[8] Thus, these complexes are so-called complex salts, which possess neutral TCNQ.[9]

## ELECTRICAL RESISTIVITIES OF THE COMPLEXES

Electrical resistivities of the complexes were measured with the compressed samples at room temperture, which is summarized in Table 2. The resistivities are in the range of 31 to $10^7$ Ωcm. In the cases of Rh complexes, the resistivities differ about 32 folds for the complexes of cis- and trans-cyclams. Relatively high conductivities were found for La-, Mn-, and Pd-complexes, all of which are assumed to be complex salts from the reflection spectra. These facts arise from the reduced Coulomb repulsion among mobile electrons.[9] The best conductor was the ammonium-type complex (31 Ωcm).

TABLE 1. Transition-metal Cation-TCNQ-Cyclam Complexes[a]

| Complexes | Yields/% | Analytical Data/%,(Calcd) C | H | N |
|---|---|---|---|---|
| Cyc $Ni^{2+}(TCNQ^-)_2$ | 45 | 60.87 (61.11) | 4.98 (4.83) | 25.20 (25.27) |
| Cyc $Cu^{2+}(TCNQ^-)_2 2H_2O$ | 59 | 57.62 (57.66) | 4.81 (5.12) | 23.61 (23.73) |
| Cyc $Zn^{2+}(TCNQ^-)_2 H_2O$ | 54 | 59.48 (58.96) | 4.69 (4.80) | 24.49 (24.29) |
| cis-Cyc $Rh^{3+}TCNQ^-(Cl^-)_2$ | 87 | 45.10 (45.69) | 4.93 (4.88) | 18.93 (19.38) |
| trans-Cyc $Rh^{3+}TCNQ^-(Cl^-)_2$ | 74 | 45.97 (45.69) | 4.65 (4.88) | 19.57 (19.38) |
| trans-Cyc $Co^{3+}(TCNQ^-)_2 Cl^-$ | 32 | 57.24 (58.08) | 4.49 (4.59) | 23.11 (23.91) |
| $(Cyc)_2 La^{3+}(TCNQ^-)_3 TCNQ$ | - | 60.41 (60.21) | 4.61 (4.76) | 24.61 (24.78) |
| $(Cyc)_2 Mn\ TCNQ_6$ | 74 | 65.89 (65.75) | 4.32 (4.32) | 26.87 (26.67) |
| $(Cyc)_2 Pd\ TCNQ_4$ | - | 62.52 (62.01) | 3.63 (3.59) | 25.34 (24.93) |
| $Cyc\text{-}2H^+(TCNQ^-)_2(TCNQ)_2$ | 26 | 68.11 (68.35) | 4.13 (4.15) | 27.03 (27.49) |

[a]Cyc=cyclam. Cyc-2H$^+$ = diprotonated cyclam at the nitrogens

TABLE 2 Electrical Resistivities of the Complexes

| Complexes | Resistivities/Ωcm |
|---|---|
| Cyc $Ni^{2+}(TCNQ^-)_2$ | $1.0 \times 10^7$ |
| Cyc $Cu^{2+}(TCNQ^-)_2 2H_2O$ | $5.5 \times 10^6$ |
| Cyc $Zn^{2+}(TCNQ^-)_2 H_2O$ | $4.2 \times 10^6$ |
| cis-Cyc $Rh^{3+}TCNQ^-(Cl^-)_2$ | $2.8 \times 10^6$ |
| trans-Cyc $Rh^{3+}TCNQ^-(Cl^-)_2$ | $8.8 \times 10^4$ |
| trans-Cyc $Co^{3+}(TCNQ^-)_2 Cl^-$ | $1.8 \times 10^3$ |
| $(Cyc)_2 La^{3+}(TCNQ^-)_3 TCNQ$ | $2.4 \times 10^3$ |
| $(Cyc)_2 Mn\ TCNQ_6$ | $5.1 \times 10^2$ |
| Cyc Pd $TCNQ_4$ | 78 |
| $Cyc\text{-}2H^+(TCNQ^-)_2(TCNQ)_2$ | 31 |

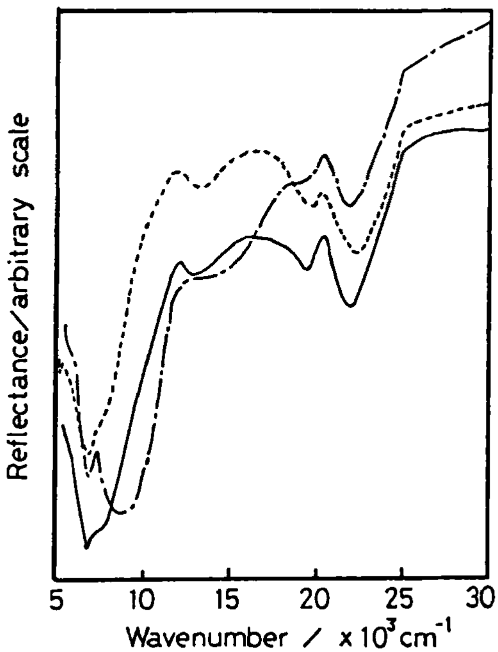



FIGURE 1. Diffuse Reflection Spectra of the Complexes.
-----$(Cyc)_2La^{3+}(TCNQ^-)_3TCNQ$, —— $(Cyc)_2Mn\ TCNQ_6$, -·—$(Cyc)_2Pd\ TCNQ_4$

References

1. T. Nogami, M. Morinaga, Y. Kanda, and H. Mikawa, Chem. Lett., 111 (1979).
2. M. Morinaga, T. Nogami, Y. Kanda, T. Matsumoto, K. Matsuoka, and H. Mikawa, Bull. Chem. Soc. Jpn., 53, 1221 (1980).
3. T. Matsumoto, T. Nogami, and H. Mikawa, Bull. Chem. Soc. Jpn., 55, (1982), in press.
4. F. Basolo, Inorg. Syn., 16, 220 (1976).
5. E. J. Bounsall and S. R. Koplich, Can. J. Chem., 48, 1482 (1970).
6. B. Bosnich, C. K. Poon, and M. L. Tobe, Inorg. Chem., 4, 1102 (1965).
7. The structural difference between cis- and trans-cyclams is that the four nitrogens are coplanar in the former isomer, and nonplanar in the latter isomer (see ref. 5).
8. J. Tanaka, M. Tanaka, T. Kawai, T. Takabe, and O. Maki, Bull. Chem. Soc. Jpn., 49, 2358 (1976).
9. L. R. Melby, R. J. Harder, W. R. Hertler, M. Mahler, R. E. Benson, and W. E. Mochel, J. Am. Chem. Soc., 84, 3374 (1962).