2452 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2452—2454 (1972) [Vol. 45, No. 8

Schiff Bases Derived from Heptane-2,4,6-trione and Ethylenediamine, and Its Copper(II) and Oxovanadium(IV) Chelates*

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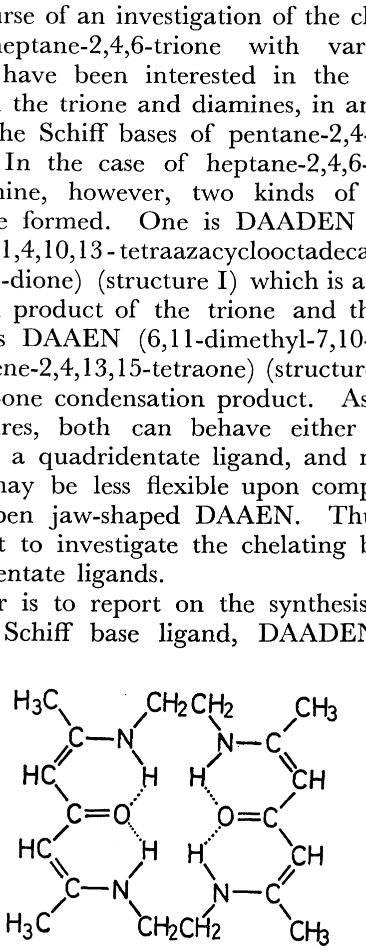
(Received October 6, 1971)

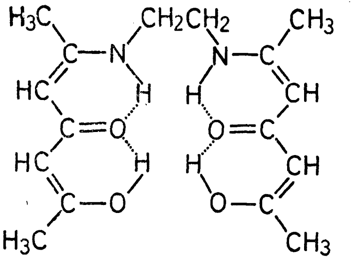
The copper(II) and oxovanadium(IV) complexes of a new Schiff base derived from heptane-2,4,6-trione and ethylenediamine were prepared. Of a macrocyclic two-to-two and an open jaw-shaped two-to-one (trione to diamine) condensation product, only the latter gave mononuclear copper(II) and oxovanadium(IV) complexes. The coordinating sites to the metal ion in each complex are discussed referring to the spectroscopic results.

In the course of an investigation of the chelate complexes of heptane-2,4,6-trione with various metal ions,[1,2] we have been interested in the Schiff base derived from the trione and diamines, in an analogous manner to the Schiff bases of pentane-2,4-dione and diamines.[3] In the case of heptane-2,4,6-trione and ethylenediamine, however, two kinds of the Schiff bases can be formed. One is DAADEN (5,9,14,18-tetramethyl-1,4,10,13-tetraazacyclooctadeca-5,8,14,17-tetraene-7,16-dione) (structure I) which is a two-to-two condensation product of the trione and the diamine. The other is DAAEN (6,11-dimethyl-7,10-diazahexadeca-6,10-diene-2,4,13,15-tetraone) (structure II) which is a two-to-one condensation product. As seen from their structures, both can behave either as a sexadentate or as a quadridentate ligand, and macrocyclic DAADEN may be less flexible upon complex formation than open jaw-shaped DAAEN. Thus, it is of great interest to investigate the chelating behavior of these multidentate ligands.

This paper is to report on the synthesis of a new macrocyclic Schiff base ligand, DAADEN, as well as the syntheses and structural studies on the mononuclear open jaw-shaped DAAEN chelates of copper(II) and oxovanadium(IV) ions.



Structure I



Structure II

Experimental

Synthesis of the Ligand. *DAADEN.* To 60 m*l* of a methanolic solution containing 10.0 g (0.07 mol) of heptane-2,4,6-trione, was added 10 m*l* of methanolic solution of 4.6 g (0.074 mol) of 98% ethylenediamine, and the mixture was warmed at 30—40°C for a few minutes. Resulting precipetate was collected by filtration, and recrystallized from a methanol-chloroform mixture to give pale yellow needles. Yield was 10.7 g; mp 215—216°C. NMR(CDCl$_3$): 1.88 ppm (12H), 3.23—3.40 ppm(8H), 4.77 ppm(4H), 10.70—11.50 ppm(4H). IR: 1625 cm^{-1} $\nu_{C=O}$(hydrogen bonded); 1580 and 1520 cm^{-1}, $\nu_{C=C}$ and $\nu_{C=N}$.

Found: C, 64.76; H, 8.53; N, 16,69%. Calcd for $C_{18}H_{28}N_4O_2$: C, 65.03; H, 8.49; N, 16.85%.

Syntheses of the Metal Chelates. *Copper(II)-DAAEN Chelates*: Into 250 m*l* of a chloroform solution containing 3.32 g (0.01 mol) of DAADEN, was added with stirring 100 m*l* of an aqueous solution of 2.0 g (0.01 mol) of cupric acetate monohydrate, and the mixture was stirred for 30 min at 18°C until a green precipitate appeared in an aqueous layer and a chloroform layer became dark violet. The green precipitate in the aqueous layer was collected by filtration, recrystallized from pyridine and dried under reduced pressure to yield green powder (1.48 g, 36.3%) which was found to be bis(heptane-2,4,6-trionato)dicopper(II), by elemental analysis and infrared spectral comparison with an authentic sample.[2]

The dark violet chloroform layer was evaporated under reduced pressure to remove the solvent, and the residual oil was dissolved again into a small amount of chlorofrom. The chloroform solution was eluted on a column of activated alumina (50 g) with the same solvent. After the solvent was distilled off from the eluate, the residual solid was recrystallized from a *n*-hexane-chloroform mixture, to yield red-violet crystalline powder, Complex A, (0.94 g, 25.5%). IR: 1720 and 1705 cm^{-1}, $\nu_{C=O}$(free); 1590 and 1520 cm^{-1}, $\nu_{C=O}$, $\nu_{C=C}$ and provably $\nu_{C=N}$.[4]

Found: C, 52.66; H, 6.20; N, 7.39%. Calcd for $C_{16}H_{22}N_2O_4Cu$: C, 52.00; H, 5.95; N, 7.30%.

Oxovanadium(IV)-DAAEN Chelate. Into a solution of 2.84 g (0.02 mol) of heptane-2,4,6-trione in 70 m*l* of methanol, were added a solution of 0.6 g (0.01 m*l*) of 98%

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* Contribution No. 260 from the Department of Oragnic Synthesis, Kyushu University

1) F. Sagara, H. Kobayashi, and K. Ueno, This Bulletin, **41**, 266 (1968).

2) F. Sagara, H. Kobayashi, and K. Ueno, This Bulletin, **45**, 794 (1972).

3) For example, K. Ueno and A. E. Martell, *J. Amer. Chem. Soc.*, **59**, 998 (1955).

4) K. Nakamoto, "Infrared spectra of inorganic and coordination compounds" 2nd Ed., Wiley-Interscience, New York, 1970.

ethylenediamine in 20 m*l* of methanol and 1.01 g (0.01 mol) of finely powdered oxovanadium hydroxide. The mixture was refluxed under a nitrogen atmosphere for 1.5 hr. The resulting green precipitate and unreacted oxovanadium hydroxide were collected by filtering the reaction mixture, and the solid mixture was treated with chloroform to dissolve the chelate. After evaporating the solvent from the chloroform solution, the green residue was recrystallized from pyridine to yield brown needles (2.07 g). When this product was dried at 64°C under $10^{-3}-10^{-4}$ mmHg, green needles, VO-DAAEN, (1.7 g, 49.5%) were obtained. IR: 3220 cm^{-1}, ν_{N-H}(hydrogen bonded); 1627 cm^{-1}, $\nu_{C=O}$(coordinated); 1595, 1555, and 1538 cm^{-1}, $\nu_{C=O}$, $\nu_{C=C}$, and $\nu_{C=N}$ of chelate ring; 980 cm^{-1}, $\nu_{V=O}$.

Found: C, 52.11;H, 6.05; N, 7.51%. Calcd for $C_{16}H_{22}N_2O_5V$: C, 51.49; H, 5.94; N, 7.51%.

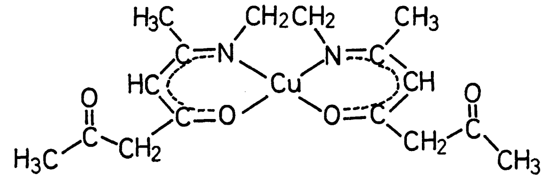
Apparatus and Measurement. IR spectra were measured with JASCO DS-301 and DS-403G spectrophotometers. The NMR spectra were recorded on a Varian A-60 instrument using TMS as an internal reference. Thermogravimetric analysis on the pyridine adduct of the oxovanadium chelate was conducted with a Shimadzu automatic recording thermobalance. The furnace temperature was raised at a rate of 3°C per minute under a nitrogen atmosphere and the weight loss was recorded automatically up to 367°C.

Results and Discussion

Quadridentate ligands derived from 1,2- or 1,3-diamines and *β*-dicarbonyl compounds have been investigated extensively, and their coordinating structure has been well established to be *N,N,O,O*,-tetracoordinate square planar. In this connection, our first attempt was to synthesize a macrocyclic sexadentateligand (DAADEN) which was a two-to-two condensation product of ethylenediamine and heptane-2,4,6-trione. The condensation reaction took place very easily in methanol, yielding an expected compound. The infrared absorption spectrum of the product does not show any band due to ν_{N-H} of free amino group, indicating that both amino groups on ethylenediamine are involved with the condensation reaction. On the other hand, the reaction of heptane-2,4,6-trione and methylamine gave 1,2,6-trimethylpyridone in a high yield,[5] and the above fact suggests the inactivity of the carbonyl group at 4-position of the trione against the condensation with amines. It is very likely, therefore, that the condensation of heptane-2,4,6-trione with diamines also takes place on the both terminal carbonyl groups of the trione, but not on the central one. These presumptions, combined with the empirical formula from the elemental analysis, indicate the structure I for DAADEN.

Our second attempt was to synthesize an open jaw-shaped sexadentate ligand (DAAEN) which was a two-to-one (trione to diamine) condensation product. However, our trials under various reaction conditions have not been successful yet. On the other hand, this particular ligand was found to be only obtainable in a form of metal chelate as described below.

Copper Chelates. Contrary to our expectation, the reaction of DAADEN with cupric ion gave no macrocyclic copper(II) chelate, but bis(heptane-2,4,6-trionato)dicopper(II) and the complex A (Cu-DAAEN). The fact that the chelate of the parent trione is obtained in a considerable yield even under such mild reaction conditions is indicative of the relative easiness of hydrolysis of DAADEN. The ligand itself is, however, fairly stable in an aqueous solution, and therefore copper(II) ion may catalyze to accelerate such hydrolysis reaction.



Structure III

As to the complex A, the infrared spectrum shows a coordinated carbonyl band at 1590 cm^{-1} and two peaks related to uncoordinated carbonyl groups at 1720 and 1705 cm^{-1}, the presence of the latter band indicating that not all of the carbonyl groups are engaged in coordination with copper ion. The result of elemental analysis also suggests the one-to-one mononuclear DAAEN chelate. Electronic spectrum of the complex A in chloroform is shown in Fig.1 along with those of the model compounds of similar coordination structures; bis(acetylacetonato)copper(II) (Cu(acac)$_2$) and bis(acetylacetone)ethylenediiminato-copper(II) (Cu-ACEN), in the same solvent. It is well known that the absorption maxima and intensity of *d-d* transition band are sensitive to the number and symmetry of donor atoms around the central metal ion, and to the ligand field strength. Thus, the close similarity of the absorption spectrum of the complex A to that of bis(acetylacetone)ethylenediiminato-copper(II), strongly suggests the N_2O_2-tetracoordinate planar structure III for the complex A. Analytical

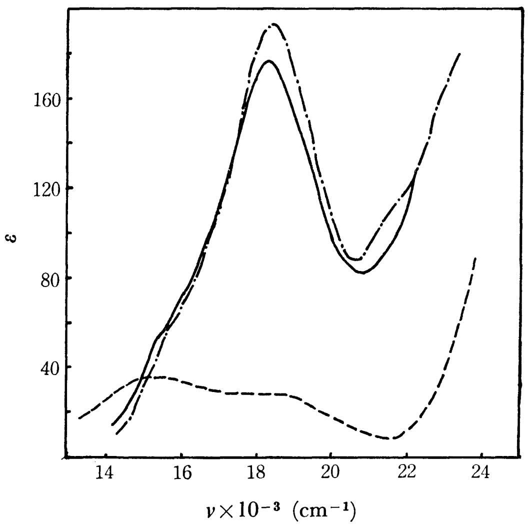


Fig. 1. Electronic absorption spectra in chloroform.
—— Complex A, Cu-DAAEN, —·— Cu-ACEN, - - - Cu(acac)$_2$.

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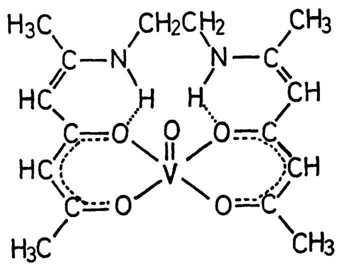
[5] S. Hunig and G. Kobrich, *Ann.*, **617**, 181 (1958).

result and infrared spectra are also consistent with this structure.

It is interesting to note that DAAEN could not be formed without the presence of copper ion and could be isolated only in a form of the metal chelate, though in a low yield. Copper(II) ion in this case may stabilize the Schiff base ligand against hydrolysis in a similar manner as in the case of bis(acetylacetone)ethylenediiminatocopper(II). This behavior of DAAEN forms a striking contrast to the macrocyclic DAADEN, of which we have been unsuccessful in obtaining the copper(II) chelate.



Structure IV

Oxovanadium(IV) Chelate. The reaction of DAADEN with oxovanadium(IV) salts in aqueous media did not give any product of definite composition. However, the reaction of heptane-2,4,6-trione and ethylenediamine with oxovanadium(IV) hydroxide under a nitrogen atmosphere yielded the metal chelate of DAAEN presumably *via* a template reaction.

The result of elemental analysis suggests the one-to-one oxovanadium(IV) chelate of DAAEN. Infrared spectrum is characterized with absorption bands due to an imino group, a coordinated carbonyl group and a V=O bond at 3220,1628, and 980 cm^{-1} respectively. The bands assignable to uncoordinated carbonyl groups are not observed.

Electronic spectrum of the VO-DAAEN chelate in chloroform is shown in Fig. 2 along with those of bis(acetylacetonato)oxovanadium(IV) (VO(acac)$_2$) and bis(acetylacetone)ethylenediiminatooxovanadium(IV) (VO-ACEN) in the same solvent. In contrast to the copper chelate, close similarity of thes pectra is noticed between the DAAEN- and the acetylacetonato-chelate, suggesting that an O_5-pentacoordinate square pyramidal structure IV is preferable to an N_2O_3 type coordination for the VO-DAAEN chelate. The structure IV is consistent with the infrared spectral evidence that no free carbonyl group is left in the chelate.

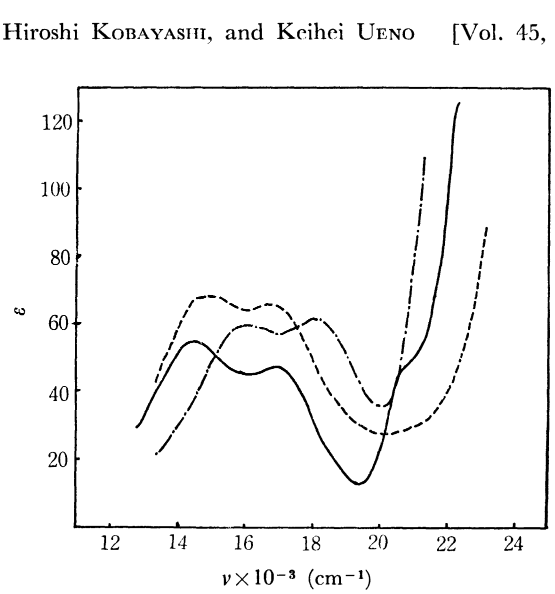


Fig. 2. Electronic absorption spectra in chloroform.
—— VO-DAAEN, —·— VO-ACEN,
- - - VO(acac)$_2$.

The reversible addition of one mole of pyridine to one mole of the chelate also indirectly supports the square pyramidal structure. When the green VO-DAAEN chelate is recrystallized from pyridine, a brown DAAEN-VO-Py, which is presumably an octahedral coordination sturcture, is obtained. Thermogravimetric analysis on the pyridine adduct showed a sudden weight decrease corresponding to the loss of one mole of pyridine per mole of the adduct at a temperature between 199 and 201°C. The substance remaining after the thermal analysis was identical with the green VO-DAAEN.

The reason why the coordination site of DAAEN differs depending upon the kind of metal ions can be explained by the soft and hard acid and base concept.[6] If one reminds that oxovanadium(IV) ion is a harder acid than copper(II) ion, and that oxygen is a harder base than nitrogen, then it is reasonable that oxovanadium(IV) ion prefers an O_4 type coordination, while copper(II) ion prefers an N_2O_2 coordination.

The authors are grateful to Messrs. Hiroshi Yamachika and Shûzo Kano for their laboratory work during the early stage of this work. They also thank the Ministry of Education for a financial support.

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6) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).