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Thiolate-bridged Metal Complexes. Nickel(II), Palladium(II), and Cobalt(III) Binuclear Complexes of 1,5-Diamino-3-pentanethiol

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A binucleating ligand with thiolate sulfur as a bridging atom, 1,5-diamino-3-pentanethiol (Hdpet) and its metal complexes, $Ni_2(dpet)_2X_2$ (X=Br, ClO_4, NO_3, BPh_4, and NCS) were synthesized. All the complexes are diamagnetic at room temperature. The Ni(II) and Pd(II) complexes assume binuclear thiolate-bridged square planar coordination. This structure is maintained even in aqueous solution. The electronic spectra of the Ni(II) complexes showed a band at $27.3\times10^3\ cm^{-1}$ corresponding to the $29.8\times10^3\ cm^{-1}$ band of $[Ni_2(dpl)_2]^{2+}$ which is characteristic of oxo-bridged Cu(II) and Ni(II) complexes and was assigned to the $p\pi(O)\rightarrow d\sigma(metal)$ transition. Several trials by different methods only resulted in the separation of a single species of Co(III) complex, $Co_2(dpet)_3(ClO_4)_3$. This was characterized as a bioctahedron facially joined at the three thiolate sulfur atoms.

In contrast to a great number of alkoxo- and phenoxo-oxygen-bridged complexes, only few thiolate-sulfur-bridged complexes have been reported,[1] though thiolate coordination is important in bioinorganic chemistry. In this paper we report the synthesis of binucleating ligand, 1,5-diamino-3-pentanethiol (Hdpet), and its nickel(II), palladium(II), and cobalt (III) complexes. This ligand has no unsaturated bond, hence no absorption in the visible and the near-ultraviolet region ($<35\times10^3\ cm^{-1}$). Thus, in the spectra of complexes with this ligand the d-d and CT bands would be easily identified in that region. This ligand is an analogue of 1,5-diamino-3-pentanol (Hdpl) whose copper(II) and nickel(II) complexes were previously reported.[2,3] The palladium(II) complex of dpl was newly prepared in this study. Thus, we can clearly see the effect of substitution of sulfur for bridging alkoxo-oxygen by comparing the properties of the dpet complexes with those of dpl analogs. The copper(II) and nickel(II) dpl complexes showed a band in the ultraviolet region which is characteristic of oxo-bridged structure and was assigned to the $p\pi(O)\rightarrow d\sigma(metal)$ transition.[2,4] It is interesting to see whether such a band is also observed in the dpet complexes.

Results and Discussion

$[Ni_2(dpet)_2]X_2$ (X=Br, ClO_4, NO_3, BPh_4, NCS). The elemental analysis data accord with the values calculated as the 1:1 complex for all the nickel complexes. The planar and binuclear structure as depicted in Fig. 1 was supposed for this series of complexes on the bases of the binucleating nature of the ligand and the analogy of the dpl complexes.[2,3] The square planar coordination was confirmed by the spectral and magnetic measurements; *i.e.*, all these complexes are diamagnetic at room temperature, and the electronic spectra show only one band in the visible region in solution ($20.6\times10^3\ cm^{-1}$, $\varepsilon=360$ in methanol) and in Nujol mull ($21.1\times10^3\ cm^{-1}$ for the perchlorate). All the $[Ni_2(dpet)_2]^{2+}$ complexes except for the tetraphenylborate are soluble and stable in water forming an orange-red solution whose spectrum is almost identical with that of the methanol solution (*cf.* Figs. 2 and 3). This fact implies that the axial coordination of water molecule is very weak and the planar binuclear structure is maintained in aqueous solution.

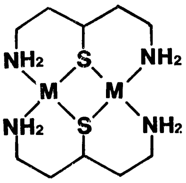


Fig. 1. $[M_2(dpet)_2]^{2+}$.

Nujol mull and powder reflectance spectra of the perchlorate, tetraphenylborate, and bromide showed the d-d band at almost the same position ($(20.9—21)\times10^3\ cm^{-1}$), but in the case of the thiocyanate the d-d band shifts to $20.0\times10^3\ cm^{-1}$. These facts imply that practically no axial coordination is present except for the thiocyanate, where a weak axial interaction with NCS^- may exist.

In the IR spectrum of $Ni_2(dpet)_2(ClO_4)_2$ there is also no indication of perchlorate coordination, either, since the splitting of the ν(Cl–O) band at about 1100 cm^{-1} is small (less than 70 cm^{-1}). The thiocyanate showed the band due to NCS^- at 2050 and 2075 cm^{-1}. This may be interpreted in terms of the assumption that one of the NCS^- ions weakly coordinates to the nickel ion while the other one is free, thus, the 2050 and 2075 cm^{-1} bands being assigned to the coordinated and the free NCS^-, respectively.[6] All these views deduced from IR data are quite consistent with those from the electronic spectra.

The band at $27.3\times10^3\ cm^{-1}$ (in methanol) should correspond to the near-ultraviolet band ($29.8\times10^3\ cm^{-1}$) of $Ni_2(dpl)_2(BPh_4)_2$ which is characteristic of alkoxo-bridged planar copper(II) and nickel(II) complexes, and was assigned to the $p\pi(O)\rightarrow d\sigma(metal)$ transition.[2,4] Thus, the $27.3\times10^3\ cm^{-1}$ band is attributable to the CT transition from $p\pi(S)$ to $d\sigma(Ni)$. Here, it is to be noted that this is the first observation of the S→Ni CT transition which corresponds to the band characteristic of alkoxo-oxygen-bridged copper (II) and nickel(II) complexes.[4] The band at $33.2\times10^3\ cm^{-1}$ (in methanol) may be assigned to the $\sigma(S)\rightarrow d\sigma(Ni)$ transition. Similar sequence of the bands was observed for Ni_2LX_2 ($L=NH_2CH_2CH_2NH(CH_2)_nS^-$,

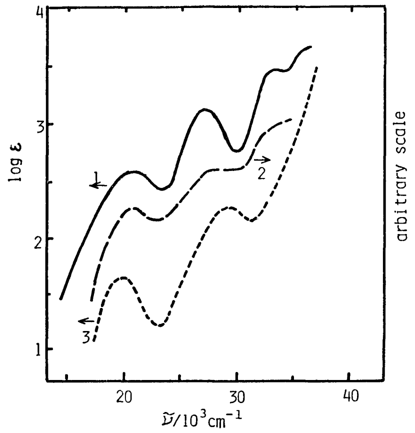


Fig. 2. Absorption spectra of $Ni_2(dpet)_2Br_2$ in methanol (1) and in Nujol mull (2), and $Ni_2(dpl)_2(Bph_4)_2$ in methanol (3).

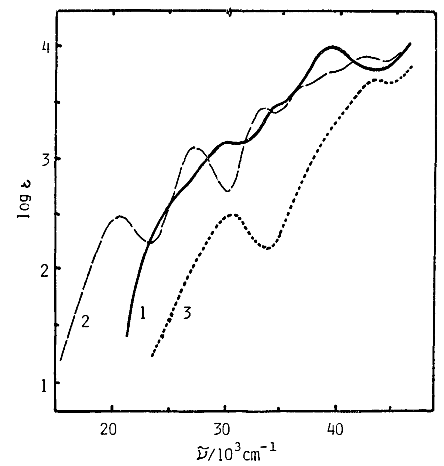


Fig. 3. Absorption spectra of $Pd_2(dpet)_2(ClO_4)_2$ (1), $Ni_2(dpet)_2(ClO_4)_2$ (2), and $Pd_2(dpl)_2(ClO_4)_2$ (3) in water.

X=Cl, Br); *e.g.*, 19.8 (ε=593), 28.2 (1510), and 32.9×10^3 cm^{-1} (5290) for n=2, X=Cl in methanol,[5] hence similar transitions can be assigned to these bands.

$Pd_2(dpet)_2(ClO_4)_2$. Infrared spectrum of this compound is nearly identical with that of the corresponding nickel analogue, indicating that the compound has a similar structure.

The electronic spectrum is, in general, much higher in intensity compared with that of $Pd_2(dpl)_2(ClO_4)_2$ and shifted to a higher frequency region compared with that of $Ni_2(dpet)_2(ClO_4)_2$ as shown in Fig. 3. The bands observed at ≈26 (shoulder), 30.3, and 35×10^3 cm^{-1} (shoulder) seem to correspond to the 20.8, 27.3, and 33.2×10^3 cm^{-1} bands of $Ni_2(dpet)_2{}^{2+}$ (*cf.* Fig. 3).

$Co_2(dpet)_3(ClO_4)_3$. Applying several different methods, and eluting the reaction products on a SP-Sephadex column, we have obtained only a single species of well defined cobalt(III) complex. The elemental analysis revealed that the crystals were formulated as $Co_2(dpet)_3(ClO_4)_3$. Since this compound is diamagnetic at room temperature, it is most likely to be a cobalt(III) complex. For the reasonable structure of this compound only the binuclear structure as depicted in Fig. 4 can be figured. It is to be remarked here that in the case of 1,3-diamino-2-propanethiol the mononuclear cis and trans 1:2 cobalt(III) complexes were obtained.[7]

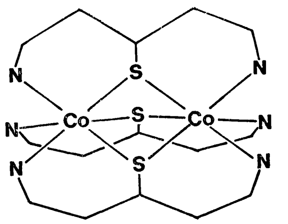


Fig. 4. The proposed structure of $[Co_2(dpet)_3]^{3+}$.

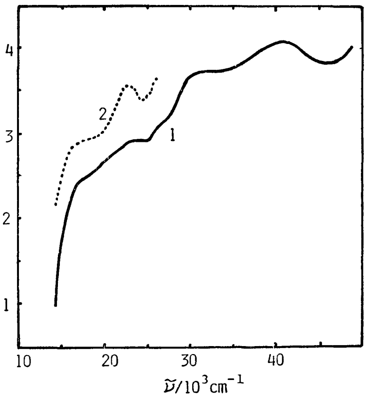
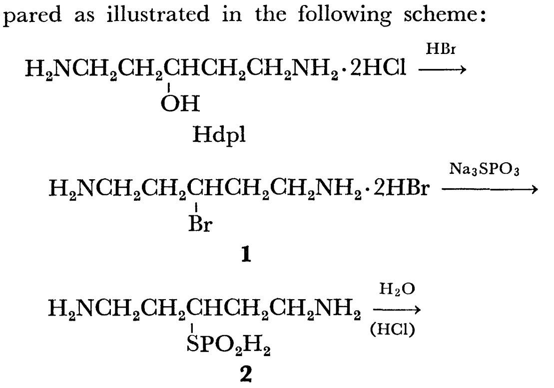


Fig. 5. Absorption spectra of $Co_2(dpet)_3(ClO_4)_3$ (1) and $[CdCo_2(mea)_6]^{2+}$ [8] (2).

The electronic spectrum of $[Co_2(dpet)_3](ClO_4)_3$ is shown in Fig. 5. This closely resembles the spectrum of $[CdCo_2(mea)_6]^{2+}$ (mea=2-aminoethanethiol) where the two *fac*-$[CoN_3S_3]$ chromophores are joined with the $[CdS_6]$ octahedron at the opposite faces.[8] The bands at 17.3×10^3 cm^{-1} (ε=280) and 23.3 (ε=791) are attributable to the spin-allowed d-d transitions, ${}^1A_{1g}\rightarrow{}^1T_{1g}$ and ${}^1A_{1g}\rightarrow{}^1T_{2g}$, respectively, in an approximation of O_h symmetry. It is known that the energy difference between the two spin-allowed bands can be a measure of the "nephelauxetic effect" of cobalt(III) complexes.[9] The value (6.3×10^3 cm^{-1}) for $[Co_2(dpet)_3]^{3+}$ is in between those for $[Co(en)_3]^{3+}$ (8.1×10^3 cm^{-1}) and $[Co(dtc)_3]$ (5.5×10^3 cm^{-1}), where dtc$^-$ denotes diethyldithiocarbamate ion. This is consistent with the proposed structure and the assignment of the bands.

Experimental

Ligand Synthesis. 1,5-Diamino-3-pentanethiol was prepared as illustrated in the following scheme:



$$\underset{\textstyle OH}{H_2NCH_2CH_2\underset{|}{C}HCH_2CH_2NH_2\cdot 2HCl} \xrightarrow{HBr}$$

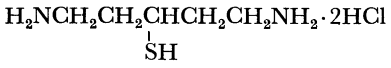
Hdpl

$$\underset{\textstyle Br}{H_2NCH_2CH_2\underset{|}{C}HCH_2CH_2NH_2\cdot 2HBr} \xrightarrow{Na_3SPO_3}$$

1

$$\underset{\textstyle SPO_2H_2}{H_2NCH_2CH_2\underset{|}{C}HCH_2CH_2NH_2} \xrightarrow[(HCl)]{H_2O}$$

2



$H_2NCH_2CH_2CH(SH)CH_2CH_2NH_2\cdot 2HCl$

3

1,5-Diamino-3-pentanol[2] (Hdpl) was converted to 3-bromo-1,5-pentanediamine (**1**) according to the standard method.[10] Conversion of (**1**) to the corresponding thiol (**3**) was best proceeded via the phosphorothioate (**2**), which was obtained by the reaction of **1** with trisodium phosphorothioate.[11]

3-Bromo-1,5-pentanediamine Dihydrobromide. A mixture of 1,5-diamino-3-pentanol dihydrochloride (50 g, 0.26 mol) and 47% hydrobromic acid (500 g, 2.9 mol) was heated in an oil bath with keeping the temperature of the bath at 145—150 °C, and 85 cm^3 of hydrobromic acid was slowly distilled at bp 125 °C. The residual solution was refluxed for 1 h and then hydrobromic acid (45 cm^3) was distilled off. This procedure was repeated additional two times and 37 cm^3 and 28 cm^3 of hydrobromic acid were recovered respectively. After refluxing the residual solution for 1 h, the bath temperature was raised to 155—160 °C and hydrobromic acid was distilled off so far as possible. In total 315 cm^3 of hydrobromic acid has been recovered. The warm residue was poured into 500 cm^3 of acetone and the resulting crystalline material was collected by filtration and dried in a vacuum desiccator. Crude yield was 83 g (92%). The sample was recrystallized from ethanol. Found: C, 18.00; H, 4.54; N, 8.32%. Calcd for $C_5H_{13}N_2Br\cdot 2HBr$: C, 17.51; H, 4.42; N. 8.17%.

1,5-Diaminopentane-3-phosphorothioic Acid. Trisodium phosphorothioate (21.6 g, 0.12 mol) was dissolved in 140 cm^3 of water under nitrogen atmosphere at room temperature and diluted with 100 cm^3 of water. To this was added 3-bromo-1,5-diaminopentane dihydrobromide (40.8 g, 0.12 mol) by portions, then *N*,*N*-dimethylformamide (120 cm^3) was added dropwise during 30 minutes at 30 °C. The mixture was further stirred for 2 h at 30 °C and the resulting light brown solution was concentrated to a small volume under reduced pressure. Addition of ethanol (800 cm^3) to the residual solution resulted white crystalline product, which was collected by filtration and washed with ethanol. The material (30 g) which contained appreciable amount of inorganic salts was used for the next reaction without purification.

1,5-Diamino-3-pentanethiol Dihydrochloride. A mixture of crude *S*-[3-amino-1-(2-aminoethyl)propyl] dihydrogenphosphorothioate (30 g) and 20% hydrochloric acid (180 g) was heated for 1 h in an oil bath at 100—110 °C under nitrogen atmosphere. The resulting clear solution was concentrated under reduced pressure and methanol (300 cm^3) was added. The precipitates yielded were filtered off and the filtrate was concentrated. Acetone (500 cm^3) was added to the residue and the mixture was kept in a refrigerator overnight. The crystalline powder was collected by filtration, washed with acetone, and dried under vacuum over P_2O_5. This highly hygroscopic material (18 g) contained inorganic salts, but it was used for complex synthesis without further purification. The pure sample was isolated as a tetraphenylborate which was recrystallized from methanol–water, mp 92 °C. Found: C, 80.08; H, 7.57; N, 3.49%. Calcd for $(C_5H_{16}N_2S)\ [B(C_6H_5)_4]_2\cdot H_2O$: C, 80.29; H, 7.39; N, 3.53%.

Complex Synthesis. *$Ni_2(dpet)_2(ClO_4)_2$*: Crude 1,5-diamino-3-pentanethiol (Hdpet·2HCl, 0.8 g, ≈4 mmol) and nickel(II) perchlorate hexahydrate (1.5 g, 4 mmol) were dissolved in 20 cm^3 of water and the pH of the solution was adjusted to ≈9 by the addition of triethylamine. The resulting deep red solution was heated on a water bath for ten minutes and undissolved material was filtered off. Addition of excess sodium perchlorate to the filtrate resulted orange-red crystals, which were collected by filtration, washed with methanol, recrystallized from water, and dried over P_2O_5 under vacuum at room temperature. Found: C, 20.55; H, 4.59; N, 9.57; Ni, 19.9%. Calcd for $Ni_2(C_5H_{13}N_2S)_2$: C, 20.61; H, 4.50; N, 9.61; Ni, 20.1%.

The bromide, thiocyanate, nitrate, and tetraphenylborate were also obtained from a warm concentrated aqueous solution of the perchlorate (above) by adding a sodium salt of the corresponding anion in excess and cooling to room temperature. The tetraphenylborate complex was recrystallized from acetone–methanol mixture and others were done from water and all dried over P_2O_5 under vacuum at room temperature.

$Ni_2(dpet)_2Br_2$: C, 21.99; H, 4.86; N, 10.18; Ni, 21.3%. Calcd for $Ni_2(C_5H_{13}N_2S)_2Br_2$: C, 22.09; H, 4.81; N, 10.30; Ni, 21.6%.

$Ni_2(dpet)_2(NCS)_2$: C, 28.82; H, 5.33; N, 16.72; Ni, 23.4%. Calcd for $Ni_2(C_5H_{13}N_2S)_2(SCN)_2$: C, 28.82; H, 5.24; N, 16.81; Ni, 23.5%.

$Ni_2(dpet)_2(NO_3)_2$: C, 23.71; H, 5.22; N, 16.43; Ni, 23.3%. Calcd for $Ni_2(C_5H_{13}N_2S)_2(NO_3)_2$: C, 23.65; H, 5.16; N, 16.55; Ni, 23.1%.

$Ni_2(dpet)_2(BPh_4)_2\cdot C_2H_5OH$: C, 67.31; H, 6.70; N, 5.16%. Calcd for $Ni_2(C_5H_{13}N_2S)_2(C_{24}H_{20}B)_2\cdot C_2H_6O$: C, 67.45; H, 6.79; N, 5.24%.

$Pd_2(dpet)_2(ClO_4)_2$ Potassium tetrachloropalladate(II) (0.48 g, 1.5 mmol) in 10 cm^3 of water was mixed with Hdpet·2HCl (0.3 g, ≈1.5 mmol) in 10 cm^3 of water and the pH of the mixture was brought to ≈9 by the addition of triethylamine at room temperature. The resulting yellow-orange precipitates were filtered off, and an excess of sodium perchlorate was added to the filtrate. The complex was obtained as pale yellow crystals, which were recrystalized from water. Found: C, 17.45; H, 3.77; N, 8.18%. Calcd for $Pd_2(C_5H_{13}N_2S_2)_2(ClO_4)_2$: C, 17.71; H, 3.86; N, 8.26%.

$Co_2(dpet)_3(ClO_4)_3$. A mixture of Hdpet·2HCl (0.6 g, ≈3 mmol) aud trisodium tricarbonatocobaltate(III) trihydrate (0.8 g, 2 mmol) in 10 cm^3 of water was heated at 70 °C for ten minutes. The initial green solution turned deep red-brown with evolution of CO_2. The solution was cooled to room temperature, filtered, and an excess of sodium perchlorate was added to the warmed filtrate. Deep red crystals which were deposited on cooling was recrystallized from water, and dried over P_2O_5 under vacuum. Found: C, 22.09; H, 4.81; N, 10.29; Co, 14.6%. Calcd for $Co_2(C_5H_{13}N_2S)_3(ClO_4)_3$: C, 22.08; H, 4.82; N, 10.30; Co, 14.4%.

$Pd_2(dpl)_2(ClO_4)_2$. To a mixture of potassium tetrachloropalladate(II) (0.9 g, 2.7 mmol) and 1,5-diamino-3-pentanol dihydrochloride (Hdpl·2HCl, 0.5 g, 2.7 mmol) in 40 cm^3 of water was added sodium carbonate (0.84 g, 8.1 mmol) by portions. The mixture was heated on a water bath until the resulting precipitates were dissolved to give a yellow solution. The hot solution was filtered and an excess of sodium perchlorate was added to the filtrate. The pale yellow precipitates were collected by filtration, washed with methanol, and recrystallized from water. Found: C, 18.65; H, 4.07; N, 8.57%. Calcd for $Pd_2(C_5H_{13}N_2O)_2(ClO_4)_2$: C, 18.59; H, 4.06; N, 8.67%.

The reaction of Hdpet·2HCl with copper(II) ion resulted in ligand oxidation, and any kind of copper complex could not be obtained so far.

References

1) J. G. Hughes and R. Robson, *Inorg. Chim. Acta*, **36**, 237 (1979); R. Kelson and R. Robson, *J. Coord. Chem.*, **6**, 235 (1979); P. Krautil and R. Robson, *ibid.*, **10**, 7 (1980).

2) I. Murase, M. Hatano, M. Tanaka, S. Ueno, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **55**, 2404 (1982).

3) Y. Nishida and S. Kida, *Mom. Fac. Sci. Kyushu Univ., Ser. C*, **13**, 35 (1981).

4) Y. Ishimura, Y. Nonaka, Y. Nishida, and S. Kida, *Bull. Chem. Soc. Jpn.*, **46**, 3728 (1973); S. Kida, Y. Nishida, and M. Sakamoto, *ibid.*, **46**, 2428 (1973); Y. Nishida, F. Numata, and S. Kida, *Inorg. Chim. Acta*, **11**, 189 (1974); Y. Nishida and S. Kida, *J. Inorg. Nucl. Chem.*, **38**, 451 (1976).

5) S. L. Rose, R. E. Hoskin, J. E. Cavaugh, C. J. Smith, and E. L. Blim, *Inorg. Chim. Acta*, **40**, 7 (1980).

6) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed Wiley-Interscience, New York (1978) pp. 270—274.

7) K. Yamanari, N. Takeshita, T. Komorita, and Y. Shimura, *Chem. Lett.*, **1981**, 861.

8) E. L. Blinn, P. Butler, K. M. Chapman, and S. Harris, *Inorg. Chim. Acta*, **24**, 139 (1977).

9) C. K. Jørgensen, *Prog. Inorg. Chem.* **4**, 73 (1962).

10) *Cf.* F. Cortese, *Org. Synth.* Coll. Vol. II, 91 (1948).

11) J. R. Piper and T. P. Johnson, *J. Org. Chem.*, **33**, 636 (1968).