The Color Isomerism of Oxovanadium(IV) Complexes with Tetradentate Schiff Base

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Synopsis. An oxovanadium(IV) complex with *N,N'*-bis(1-methyl-2-bromo-3-oxobutylidene)ethylenediamine gave green and yellow forms in the solid state, depending upon the solvents used for recrystallization. A polymeric structure was proposed for the yellow form.

As has been reviewed elsewhere,[1-3] there have been a considerable number of spectroscopic and magnetic studies of oxovanadium(IV) complexes. Almost all complexes are blue or blue-green and exhibit strong V=O stretching frequencies around 1000 cm^{-1}. On the other hand, oxovanadium(IV) complexes of salicylideneamine, β-thioxo ketones, and dithiophosphinic acids with electron-withdrawing substituents,[4-6] and *N,N'*-disalicylidenepropylenediamine,[7,8] are yellow and shift their V=O bands to lower frequencies (around 900 cm^{-1}). The shift in the V=O stretching frequencies has been considered to be an indication of an oxygen bridging, V–O–V, polymeric-chain formation.[5,7,9] Recently, the yellow color and low V=O frequencies of oxovanadium(IV) complexes with some bidentate Schiff bases were explained in terms of distorted trigonal bipyramidal structure.[10] In the trigonal bipyramid, the three oxygen and vanadium atoms are on the equatorial plane, while the two nitrogen donors occupy axial positions. We wish to report here that an oxovanadium(IV) complex with *N,N'*-bis(1-methyl-2-bromo-3-oxobutylidene) ethylenediamine (VO(L-Br)) yields two color isomers in the solid state.

Experimental

Syntheses. [*N,N'*-Bis(1-methyl-3-oxobutylidene)ethylenediaminato]oxovanadium(IV) (VO(L)) was synthesized according to the method reported by Martin *et al.*[11]

[N,N'-Bis(1-methyl-2-bromo-3-oxobutylidene)ethylenediaminato]-oxovanadium(IV) (VO(L-Br)): *N*-Bromosuccinimide (1.8 g) was added to 20 cm^3 of a dichloromethane solution of VO(L) (1.4 g) at 0 °C, and the mixture was stirred below 0 °C for 20 min. After small amounts of precipitates had been filtered off, the filtrate was concentrated to 2—3 cm^3 under reduced pressure. The precipitates were subsequently obtained by the addition of adequate amounts of methanol. The yellow needles were recrystallized from dichloromethane (yield, 65%); IR: 902 cm^{-1} (V=O). Found: C, 32.51; H, 3.59; N, 6.69%. Calcd for $C_{12}H_{16}N_2O_3Br_2V$: C, 32.24; H, 3.66; N, 6.27%. An yellow [*N,N'*-bis(1-methyl-2-chloro-3-oxobutylidene)ethylenediaminato]oxovanadium(IV) (VO(L-Cl)) complex was synthesized using *N*-chlorosuccinimide instead of *N*-bromosuccinimide (yield, 67%); IR: 892 cm^{-1} (V=O). Found: C, 39.94; H, 4.13; N, 7.53%. Calcd for $C_{12}H_{16}N_2O_3Cl_2V$: C, 40.24; H, 4.51; N, 7.82%. Hydrogen chloride was bubbled through a dichloromethane solution of VO(L-Cl) for a few min to obtain a free ligand. The ligand thus precipitated was separated out; it was washed with water and subsequently with ethanol. On the other hand, no free L-Br ligand was obtained because of the decomposition of VO(L-Br) with hydrogen chloride.

Adducts of VO(L-Br) and VO(L-Cl) with 1-Methylimidazole: A 5 cm^3 portion of 1-methylimidazole was added to 20 cm^3 of a dichloromethane solution containing 1.3 g of VO (L-Br). After the solution had been refluxed for a few min, it was condensed to 2—3 cm^3. The brown adduct was precipitated by the addition of adequate amounts of hexane and subsequently washed with ether (yield, 68%); IR: 959 cm^{-1} (V=O). Found: C, 35.94; H, 4.14; N, 10.90%. Calcd for $C_{16}H_{22}N_4O_3Br_2V$: C, 36.31; H. 4.20; N, 10.59%. A brown adduct of the chloro derivative was obtained by a method similar to that described above (yield, 75%); IR: 959 cm^{-1} (V=O). Found: C, 43.36; H, 4.95; N, 12.67%. Calcd for $C_{16}H_{22}N_4O_3Cl_2V$: C, 43.65; H, 5.04: N, 12.73%.

Measurements. The infrared spectra were measured using nujol mull methods, on a Hitachi 215 spectrophotometer. The electronic spectra in sloution and in the solid state were measured on a Hitachi 124 spectrotometer and a Shimadzu spectrophotometer Model MPS-5000 respectively. The NMR spectra were recorded with a JEOL-MH 100 spectrophotometer at a frequancy of 100 MHz. The chemical shifts were determined in ppm, using TMS as the internal standard. The ESR spectra (X-band) of polycrystalline samples were obtained on a JEOL-1X apparatus. The X-ray powder diffraction analyses were carried out on a Toshiba ADG-301 apparatus.

Results and Discussion

Structures of Schiff-base Ligands. An NMR spectrum of the free L-Cl ligand eliminated from VO(L-Cl) shows three proton signals in 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2); δ=2.16 (12H, d, CH_3), 3.36 (4H, m, CH_2), and 11.40 ppm (2H, broad s, OH). An unsubstituted free ligand, L, also shows four proton signals in TCE-d_2 at 1.86 (12H, d, CH_3), 3.30 (4H, m, CH_2), 4.92 (2H, s, CH), and 10.92 ppm (2H, broad s, OH). The signals of the methine protons in L disappeared in the chloro derivative, indicating the chlorination on the 2-position carbon of the complex. All the proton signals of the chloro derivative were shifted to a lower magnetic field compared with those of L. This tendency is attributable to an inductive effect of the chlorine atom. The bromination must also occur on the 2-position carbon.

Isolation of the Green and Yellow Forms. The yellow form was obtained by the recrystallization of the VO(L-Br) complex from dichloromethane, and the green, from tetrahydrofuran. However, the VO(L-Cl) complex only gave the yellow form upon recrystallization from both dichloromethane and tetrahydrofuran. On the other hand, the green form of VO(L) was easily recrystallized from common organic solvents, though the yellow was not obtained at all. The yellow forms seem to be easily isolated according to an increase in the electron negativities of the substituents. In the case of

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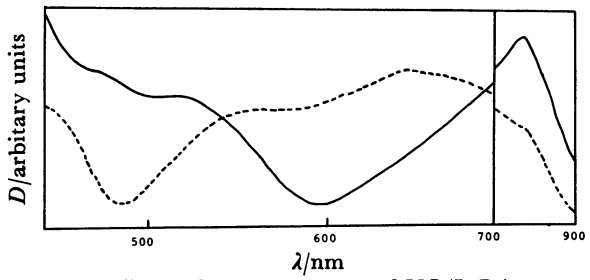

Fig. 1. Diffuse-reflectance spectra of VO(L-Br).
——: Yellow form, ------: green form.

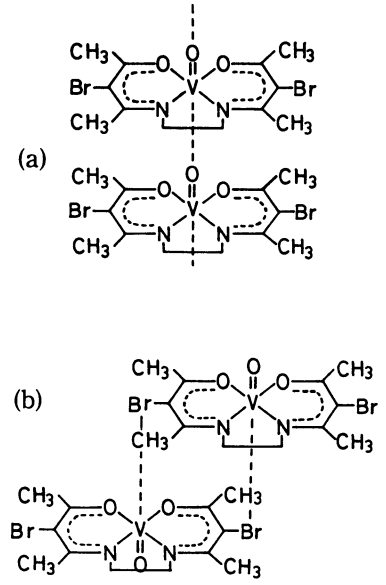

Fig. 2. The proposed structures for the yellow VO(L-Br) form.

VO(L-Br), the thermodynamic stabilities of the green and yellow forms might be similar, so that the two forms can be individually isolated by selecting appropriate solvents for recrystallization.

IR, Electronic, ESR, and X-Ray Powder Spectra. The V=O stretching frequencies of the green and yellow forms appear at *ca.* 980 and *ca.* 900 cm^{-1} respectively. This shift to lower frequencies for the yellow forms is in accord with the previously reported data for the yellow polymeric oxovanadium(IV) complexes.[4-8] The V=O stretching frequencies (959 cm^{-1}) of the 1-methylimidazole adducts lie between the values for the green and yellow forms. Both the green and yellow forms of the bromo derivative are dark green in common organic solvents, and they exhibit the same electronic spectra. The diffuse-reflectance spectra of VO(L-Br) are shown in Fig. 1. The spectrum of the yellow form significantly differs from that of the green in the solid state; the absorption band around 660 nm of the green form disappears in the yellow. The spectrum of the yellow VO(L-Br) form is similar in pattern to that of the yellow polymeric oxovanadium(IV) complex with β-thioxo ketone.[5] The ESR spectra for the green and yellow forms of VO(L-Br) were obtained in the powdered solid state at room temperature with no hyperfine structures. The g_0 value (1.972) of the yellow form is smaller than that of the green (g_0=1.984). This suggests that the electron delocalization increases in going from the green form to the yellow. The ESR spectra of VO(L-Br) diluted with Ni(II)(L) were also measured, but no clear hyperfine structures were obtained. In the X-ray powder-diffraction spectra of VO(L-Br), the peak at 14.5° of the green form became weak and a new intense peak appeared at 9.3° in the yellow. This shows different crystal forms between the green and yellow isomers.

Structure of the Yellow Form. A polymeric or distorted trigonal bipyramidal structure might be proposed for the yellow form, judging from previous reports.[5,7,9,10] The distorted trigonal bipyramid reported for the bidentate Schiff-base complexes seems difficult for the present tetradentate Schiff-base complex because of its steric hindrance. Either of the structures in Fig. 2 would be possible for the yellow form. The nitrogen atom of 1-methylimidazole must be coordinated to the vanadium(IV) ion more strongly than the bromine atom. Thus, the V=O stretching frequency of the adduct should be shifted to a lower frequency compared with that of the dimer, in which the vanadium(IV) ion is coordinated by bromine (Fig. 2b). However, the V=O stretching frequency of the adduct is higher than that of the yellow form of VO(L-Br). Therefore, the (a) structure seems more reasonable for the yellow form.

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