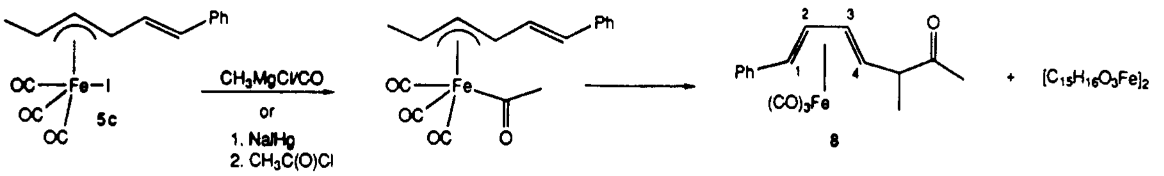
Scheme II



to dryness, and the residue was purified by chromatography on silica gel using petroleum ether–ether.

(η^3-1,5-Me$_2$ped)Fe(CO)$_3$Cl (2a): yield 26%; orange-red oil; ^{1}H NMR (CDCl$_3$; 250 MHz) 6.29 (sext, H5, $J_{5,\mathrm{Me}} = 6.5$, $J_{4,5} = 15.2$), 5.89 (m, H4, $J_{4,\mathrm{Me}} = 1.5$), 4.99 (t, H2, $J_{1,2} = 12.2$, $J_{2,3} = 12.6$), 4.68 (t, H3, $J_{3,4} = 10.5$), 4.03 (sext, H1, $J_{1,\mathrm{Me}} = 6.3$), 2.00 (d, Me at C1), 1.80 (dd, Me at C5); ^{13}C NMR (CDCl$_3$, 75.5 MHz) 207.9, 205.4, 204.2 (CO's), 133.1, 131.1 (C4,5), 101.2, 90.5, 82.2 (C1–3), 20.1, 18.7 (Me's); IR (CHCl$_3$) 2084, 2035, 2000 cm^{-1}; HRMS, $C_{10}H_{11}O_3FeCl$ (M$^+$) requires 269.9746 (not observed), $C_{10}H_{11}O_3Fe$ (M – Cl) requires 235.0058 (found 235.0052), $C_9H_{11}O_2Fe$ (M – Cl – CO) requires 207.0108 (found 207.0074), $C_9H_{11}O_2Fe$ (M – Cl – 2 CO) requires 179.0159 (found 179.0156). The dimer [$C_7H_{11}Fe(CO)_3$]$_2$ (3) was isolated in 50% yield from this reaction.

(η^3-1,5-Me$_2$ped)Fe(CO)$_3$Br (2b): yield 74%; red-brown oil; ^{1}H NMR (CDCl$_3$; 250 MHz) 6.26 (sext, H5, $J_{5,\mathrm{Me}} = 6.8$, $J_{4,5} = 15.3$), 5.81 (m, H4, $J_{4,\mathrm{Me}} = 1.5$), 4.88 (t, H3, $J_{3,4} = 9.5$, $J_{2,3} = 12.3$), 4.76 (t, H2, $J_{1,2} = 11.3$), 4.19 (sext, H1, $J_{1,\mathrm{Me}} = 6.3$), 1.94 (d, Me at C1), 1.78 (dd, Me at C5); ^{13}C NMR (CDCl$_3$, 75.5 MHz) 209.6, 205.5, 204.3 (CO's), 132.9, 131.1 (C4,5), 100.7, 87.6, 79.1 (C1–3), 20.2, 18.7 (Me's); IR (CHCl$_3$) 2076, 2029, 2001 cm^{-1}; HRMS, $C_{10}H_{11}O_3FeBr$ (M$^+$) requires 313.9240 + 315.9219 (found 313.9267 + 315.9234), $C_9H_{11}O_2FeBr$ (M – CO) requires 285.92921 + 287.9270 (found 2852.9275 + 287.9281), $C_8H_{11}OFeBr$ (M – 2 CO) requires 257.9342 + 259.9321 (found 257.9359 + 259.9339). The dimer 3 was isolated in 14% yield from this reaction.

(η^3-1,5-Me$_2$ped)Fe(CO)$_3$I (2c): yield 76%; red-brown oil; ^{1}H NMR (CDCl$_3$; 250 MHz) 6.23 (sext, H5, $J_{5,\mathrm{Me}} = 6.6$, $J_{4,5} = 15.3$), 5.78 (m, H4, $J_{4,\mathrm{Me}} = 1.5$), 5.19 (t, H3, $J_{3,4} = 10.1$, $J_{2,3} = 12.6$), 4.45 (m, H1,2), 1.90 (d, Me at C1, $J_{1,\mathrm{Me}} = 5.5$), 1.79 (dd, Me at C5); ^{13}C NMR (CDCl$_3$, 75.5 MHz) 210.8, 206.8, 205.5 (CO's), 132.3, 131.1 (C4,5), 995, 82.4, 73.6 (C1–3), 20.3, 18.5 (Me's); IR (CHCl$_3$) 2067, 2018, 2000 cm^{-1}; HRMS, $C_{10}H_{11}O_3FeI$ (M$^+$) requires 361.9102 (found 361.9089), $C_9H_{11}O_2FeI$ (M – CO) requires 333.9153 (found 333.9146), $C_8H_{11}OFeI$ (M – 2 CO) requires 305.9204 (found 305.9204). The dimer 3 was isolated in 9% yield from this reaction.

(η^3-1-Me-5-Ph-ped)Fe(CO)$_3$Cl (5a): yield 32%; orange-brown crystals; ^{1}H NMR (CDCl$_3$; 250 MHz) 7.40 (m, Ph), 7.14 (d, H5, $J_{4,5} = 15.5$), 6.60 (dd, H4, $J_{3,4} = 10.3$), 5.21 (t, H2, $J_{2,3} = 12.6$, $J_{1,2} = 11.6$), 4.91 (t, H3), 4.18 (sext, H1, $J_{1,\mathrm{Me}} = 6.4$), 2.06 (d, Me); ^{13}C NMR (CDCl$_3$, 62.9 MHz) 207.9, 205.3, 203.7 (CO's), 136.5, 135.0, 129.5, 128.9, 128.7, 126.6 (C4,5, Ph), 102.2, 90.3, 83.1 (C1–3), 20.2 (Me); IR (CHCl$_3$) 2085, 2039, 2003 cm^{-1}. Anal. Calcd for $C_{15}H_{13}O_3ClFe$: C, 54.17; H, 3.94; Cl, 10.66. Found: C, 53.89; H, 3.96; Cl, 10.47. This reaction also produced 46% of the dimer [$C_{15}H_{13}O_3Fe$]$_2$ (7) and 13% of the 1-phenyl 5-methyl isomer 6a.

(η^3-1-Me-5-Ph-ped)Fe(CO)$_3$Br (5b): yield 56%; red-brown crystals; ^{1}H NMR (CDCl$_3$; 250 MHz) 7.40 (m, Ph), 7.12 (d, H5, $J_{4,5} = 15.5$), 6.56 (dd, H4, $J_{3,4} = 10.0$), 5.12 (t, H3, $J_{2,3} = 12.1$), 5.01 (t, H2, $J_{1,2} = 11.5$), 4.38 (sext, H1, $J_{1,\mathrm{Me}} = 6.5$), 2.02 (d, Me); ^{13}C NMR (CDCl$_3$, 62.9 MHz) 209.4, 205.4, 203.8 (CO's), 136.5, 134.7, 128.9, 128.7, 128.5, 126.6 (C4,5 Ph), 101.6, 87.2, 79.9 (C1–3), 20.2 (Me); IR (CHCl$_3$) 2079, 2033, 2001 cm^{-1}. Anal. Calcd for $C_{15}H_{13}O_3BrFe$: C, 47.49; H, 3.48; Br, 21.20. Found: C, 47.81; H, 3.46; Br, 21.41. This reaction also produced 21% of the dimer 7 and 9% of the 1-phenyl 5-methyl isomer 6a.

(η^3-1-Me-5-Ph-ped)Fe(CO)$_3$I (5c): yield 49%; red-brown crystals; ^{1}H NMR (C$_6$D$_6$; 250 MHz) 7.21 (m, Ph), 6.82 (d, H5, $J_{4,5} = 15.5$), 6.11 (dd, H4, $J_{3,4} = 10.5$), 5.40 (t, H3, $J_{2,3} = 12.5$), 4.46 (sext, H1, $J_{1,\mathrm{Me}} = 6.3$), 3.75 (t, H2, $J_{1,2} = 12.0$), 1.30 (d, Me); ^{13}C NMR (CDCl$_3$, 62.9 MHz) 206.7, 205.1, 203.3 (CO's), 136.5, 134.2, 128.9, 128.8, 128.4, 126.65 (C4,5, Ph), 100.6, 81.9, 74.5 (C1–3), 20.2 (Me); IR (CHCl$_3$) 2069, 2023, 2000 cm^{-1}. Anal. Calcd for $C_{15}H_{13}O_3IFe$: C, 42.49; H, 3.09; I, 29.93. Found: C, 42.03; H, 3.43; I, 30.18. This reaction also produced 11% of the dimer 7 and 27% of the 1-phenyl 5-methyl isomer 6a.

Synthesis of (η^4-1-Ph-5-Ac-1,3-hxd)Fe(CO)$_3$ (8). a. Via Reduction of 5c with Na/Hg. **5b** (0.15 g, 0.46 mmol) was dissolved in 15 mL of THF. Na–Hg was added to the mixture, and the reaction mixture was stirred at room temperature for 3 h. The resulting solution was filtered through Celite and then added to a solution of acetyl chloride (0.28 mL, 3.86 mmol) at −78 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 15 h. Filtration through Celite and removal of solvent left an oil that was purified by column chromatography on silica gel. The desired product, **8**, was isolated as a yellow solid in 21% yield: ^{1}H NMR (CDCl$_3$; 500 MHz) 7.20 (m, Ph), 5.79 (dd, H2, $J_{1,2} = 9.2$), 5.19 (dd, H3, $J_{3,4} = 8.7$), 2.59 (m, H5, $J_{5,\mathrm{Me}} = 6.8$), 2.24 (s, acetyl Me), 2.14 (d, H1), 1.41 (br t, H4, $J_{4,5} = 9.3$), 1.33 (d, Me at C5); ^{13}C NMR (CDCl$_3$; 125.8 MHz) 211.3 (CO), 209.2 (C═O), 139.2, 128.2, 127.7, 126.0 (Ph), 82.1, 80.2 (C2,3), 61.2, 60.8 (C1,4), 51.7 (C5), 28.4 (Ac Me), 21.5 (Me at C5); IR (CHCl$_3$) 2047, 1993, 1716 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_4Fe$: C, 60.03; H, 4.74. Found: C, 60.05; H, 5.01. The reaction also gave a 37% yield of the dimer [($C_{15}H_{13}$)FeO$_3$]$_2$ (7).

b. Via Reaction of 5c with CH$_3$MgCl and CO. A solution of **5b** (0.18 g, 0.54 mmol) in 20 mL of THF was cooled to −78 °C. CH$_3$MgCl (0.20 mL of a 3.0 M solution) was added dropwise by syringe. The vessel was placed under an atmosphere of CO, and the mixture was warmed to room temperature and stirred for 15 h. After filtration through Celite, the solvent was removed. Purification by chromatography on silica gel gave an 8% yield of **8** along with a 50% yield of **7**.

Structure Determination of 5b. Red-brown needles of $C_{15}H_{13}O_3BrFe$ were grown in petroleum ether–diethyl ether. Properties of the crystal and details of structure collection are provided in Table III. Three-dimensional intensity data were collected on a Syntex P2$_1$ automated diffractometer with a graphite detector. A combination of Patterson and difference Fourier techniques provided the locations of all non-hydrogen atoms, which were refined with anisotropic thermal parameters by using full-matrix least-squares methods. The hydrogen atoms were included in the refinement at fixed idealized positions and were treated isotropically. The refinement converged to conventional factors $R_1 = 0.035$ and $R_2 = 0.046$.

Acknowledgment. This research was supported by an Atlantic Richfield Foundation Grant from the Research Corp. and by the National Science Foundation (Grant No. CHE-8705490).

Supplementary Material Available: Tables of analytical data for **3**, **6a–c**, **7**, and the 1-methyl-5-isopropylpentadienyl system and anisotropic and isotropic temperature factors for **5b** (4 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Air-Stable Chromium(II) Complexes with 1,4,8,11-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane

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Received December 23, 1987

Recently, Kida et al. prepared the octadentate ligand 1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec) together with several of its metal complexes.[2-7] All the

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(2) Murase, I.; Mikuriya, M.; Sonoda, H.; Kida, S. *J. Chem. Soc., Chem. Commun.* **1984**, 692.

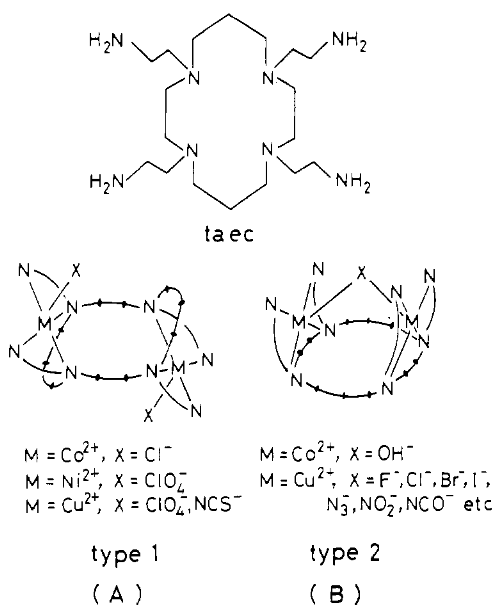

Figure 1. Coordination modes of taec.

complexes obtained were binuclear (metal:ligand = 2:1). For these complexes two types of coordination modes are known: one is the trans-III form[8] concerning the cyclam ring (type 1, Figure 1A) as found in Cu$_2$(taec)(ClO$_4$)$_4$[2], and the other is the trans-I form[8] (type 2, Figure 1B) as found in Cu$_2$(taec)Br(ClO$_4$)$_3$.[3] In the course of the investigation, the cobalt(II) complexes were found to be very resistant to oxidation.[3] For example, Co$_2$(taec)Cl$_2$(BPh$_4$)$_2$ (type 1) and Co$_2$(taec)OH(ClO$_4$)$_3$ (type 2) are not oxidized even by strong oxidizing reagents such as hydrogen peroxide and Ce^{4+}. This may be attributed to the fact that in taec complexes each metal center cannot take the six-coordination favorable for cobalt(III) because of the steric hindrance of the ligand.[3] In fact, no six-coordinated complex with this ligand has been obtained thus far. Besides cobalt(III), chromium(III) also favors six-coordination. In general, chromium(II) compounds are very easily oxidized by air. Only a few examples of air-stable chromium(II) compounds are known at present.[9-12] Therefore, we attempted to synthesize air-stable chromium(II) complexes using taec.

Experimental Section

Preparation. The preparative method for taec was already described in preceding papers.[2,3] The starting materials CrCl$_2$·4H$_2$O and CrBr$_2$·6H$_2$O were prepared by the literature method[13] under an argon atmosphere. Synthesis and isolation of chromium(II) complexes were carried out under an argon atmosphere by means of the Schlenk technique. Solvents were degassed by freeze–pump–thaw techniques prior to use.

Cr$_2$(taec)Cl$_4$. To a solution of CrCl$_2$·4H$_2$O (488 mg, 2.5 mmol) in methanol (30 mL) was added a solution of taec (373 mg, 1 mmol) in methanol (30 mL). The solution immediately changed from pale blue to dark blue. The solution was stirred vigorously for ca. 20 s. In a few minutes, blue microcrystals were deposited. After 6 h, the crystals were collected, washed with methanol twice, and desiccated in vacuo for 6 h. Anal. Calcd for C$_{18}$H$_{44}$N$_8$Cl$_4$Cr$_2$: C, 34.96; H, 7.17; N, 18.12; Cl, 22.93; Cr, 16.82. Found: C, 34.67; H, 7.28; N, 17.68; Cl, 22.09; Cr, 16.27.

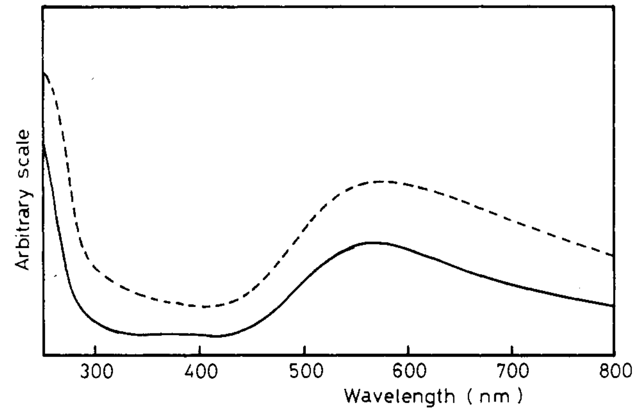

Figure 2. Diffuse-reflectance spectra of Cr$_2$(taec)Cl$_4$ (solid line) and Cr$_2$(taec)Br$_4$ (dotted line).

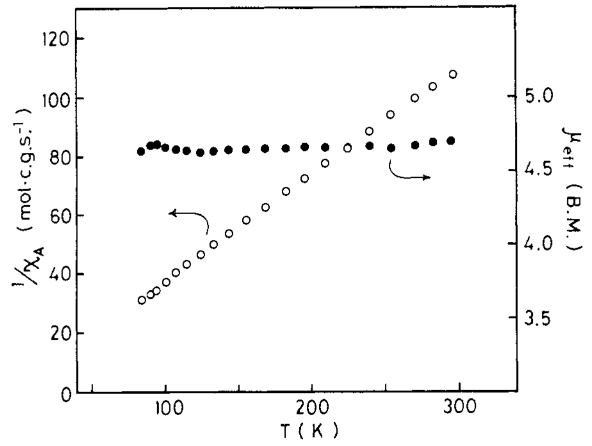

Figure 3. Magnetic moments and reciprocal susceptibilities of Cr$_2$(taec)Cl$_4$ vs temperature.

Cr$_2$(taec)Br$_4$. The complex was obtained as blue microcrystals in the same way as for Cr$_2$(taec)Cl$_4$ except CrBr$_2$·6H$_2$O was used instead of CrCl$_2$·4H$_2$O. Anal. Calcd for C$_{18}$H$_{44}$N$_8$Br$_4$Cr$_2$: C, 27.15; H, 5.57; N, 14.07; Br, 40.14; Cr, 13.06. Found: C, 27.38; H, 5.87; N, 13.80; Br, 39.72; Cr, 12.24.

Physical Measurements. Infrared spectra were measured on KBr disks with a Hitachi 295 infrared spectrophotometer. Since the complexes were not soluble in any solvents, UV–visible spectra were obtained by the diffuse-reflectance technique using a Shimadzu MPS-2000 multipurpose recording spectrophotometer. Magnetic susceptibilities were measured by the Faraday method over the temperature range 80–300 K and calibrated by using [Ni(H$_2$NCH$_2$CH$_2$NH$_2$)$_3$]S$_2$O$_3$. Diamagnetic corrections were made with Pascal's constants. Effective magnetic moments were calculated from the equation $\mu_{\text{eff}} = 2.828(\chi_A T)^{1/2}$, where χ_A denotes the atomic magnetic susceptibility.

Elemental Analyses. Carbon, hydrogen, and nitrogen analyses were carried out at the Chemical Materials Center, Institute for Molecular Science. The chromium contents were determined spectrophotometrically as Cr$_2$O$_7^{2-}$ at 350 nm after oxidizing the complexes with hot alkaline hydrogen peroxide[14] and adjusting the pH to 1. The chlorine and bromine contents were determined by a gravimetric method.

Results and Discussion

The results of elemental analyses are consistent with the formula Cr$_2$(taec)X$_4$ (X = Cl, Br). Both compounds were insoluble in common organic solvents and irreversibly hydrolyzed in water, forming pale green amorphous precipitates. As shown in Figure 2, the diffuse-reflectance spectra of both complexes closely resemble each other. The broad bands centered at ca. 575 nm may be assigned to the d–d band characteristic of high-spin planar N$_4$ chromium(II) complexes. For example, the reflectance spectrum

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(3) Murase, I.; Mikuriya, M.; Sonoda, H.; Fukuda, Y.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1986**, 953.

(4) Kida, S.; Murase, I.; Harada, C.; Daizeng, L.; Mikuriya, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2595.

(5) Mikuriya, M.; Kida, S.; Murase, I. *J. Chem. Soc., Dalton Trans.* **1987**, 1261.

(6) Mikuriya, M.; Kida, S.; Murase, I. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1355.

(7) Mikuriya, M.; Kida, S.; Murase, I. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1681.

(8) Bosnish, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.

(9) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

(10) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(11) Ardon, M.; Bino, A.; Hall, M. B. *Inorg. Chem.* **1984**, *23*, 3450. Kok, R. A.; Hall, M. B. *Inorg. Chem.* **1985**, *24*, 1542.

(12) Broderick, W. E.; Pressrich, M. P.; Geiser, U.; Willett, R. D.; Legg, J. I. *Inorg. Chem.* **1986**, *25*, 3372.

(13) Holah, D. G.; Fackler, J. P., Jr. *Inorg. Synth.* **1967**, *10*, 26.

(14) Haupt, G. W. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1952**, *40*, 2321. Deutsch, E.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1532.

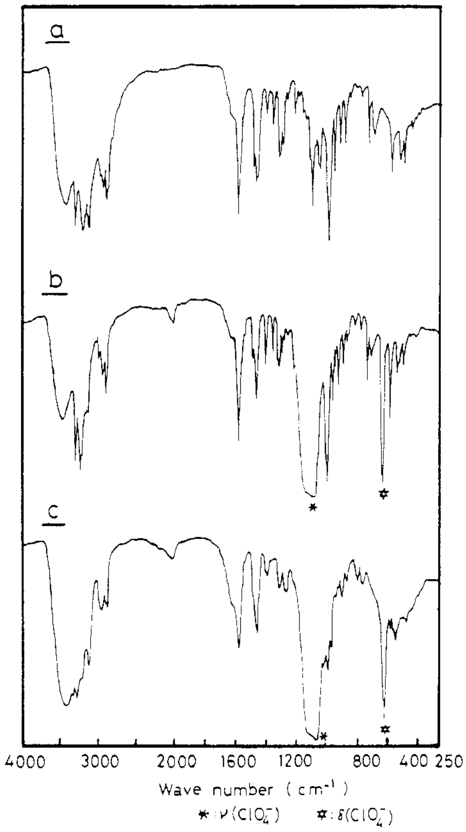

Figure 4. Infrared absorption spectra of (a) $Cr_2(taec)Cl_4$, (b) $Cu_2(taec)(ClO_4)_4$ (type 1), and (c) $Cu_2(taec)Br(ClO_4)_3$ (type 2).

of $Cr(en)_2I_2$, where en denotes ethylenediamine, has a corresponding band at 550 nm with a shoulder at 690 nm.[15] As shown in Figure 3, $Cr_2(taec)Cl_4$ obeys Curie's law and the effective magnetic moments are almost constant in the temperature range 85–300 K. The values of the effective magnetic moments, $\mu_{eff} = 4.70\ \mu_B$ (at 297 K) and $4.63\ \mu_B$ (at 85 K), were consistent with those of a chromium(II) ion of high spin state. The bromide also obeys Curie's law: $\mu_{eff} = 4.53\ \mu_B$ (at 297 K) and $4.53\ \mu_B$ (at 85 K). These results clearly indicate that magnetic interaction between the chromium(II) ions is very weak for both complexes.

As expected, the complexes are stable in dry air; no appreciable color change was observed for 1 month in dry air at ambient temperature. When exposed to moisture-saturated air, however, the compounds were tinged with brown in several minutes and became almost black in 2 h. A few air-stable binuclear chromium(II) complexes have been reported recently.[9-12] Cotton and his co-workers demonstrated that $Cr_2(hmp)_4$ (where Hhmp = 2-hydroxy-6-methylpyridine) was stable in dry air but was oxidized gradually in moist air after ca. 10 days.[9,10] Ardon et al. reported the compounds $[Cr_2(gly)_4X_2]X_2$ (where gly = zwitterionic glycine and X = Cl, Br), which were quite stable toward atmospheric oxidation in the solid state.[11] The mononuclear chromium(II) bis(nicotinate) complex *trans*-$[Cr(nic\text{-}N)_2(H_2O)_4]$ (where nic-N^- is N-coordinated nicotinate ion), reported by Broderick et al. was also stable in air. The remarkable stability of $[Cr_2(gly)_4X_2]X_2$ and *trans*-$[Cr(nic\text{-}N)_2(H_2O)_4]$ was attributed to the tight hydrogen bondings within the crystal lattice.[11,12] The binuclear complexes $Cr_2(hmp)_4$ and $[Cr_2(gly)_4X_2]X_2$ have a quadruple Cr–Cr bond, which should substantially contribute to the stability. However, in the case of our complexes, neither direct Cr–Cr bonding nor very strong hydrogen bondings like those of the above complexes are likely to exist. Hydrogen bondings much stronger than those in $Cr(en)_2I_2$, which readily undergoes air oxidation, cannot be expected for our complexes. Thus, the stability of our complexes toward air may be attributed to the steric effect of the taec ligand as observed for cobalt(II) taec complexes.

All attempts to obtain single crystals for X-ray diffraction have been unsuccessful so far. In order to elucidate the structure of the complexes, their infrared spectra were compared with those of copper(II) taec complexes whose structures were already known. It was shown in a preceding paper[4] that the type of structure of taec complexes could be diagnosed by comparing IR spectra. As shown in Figure 4, the IR spectral pattern of $Cr_2(taec)Cl_4$ is very similar to that of $Cu_2(taec)(ClO_4)_4$ (type 1), except for the absorption due to ClO_4^-, but is substantially different from that of $Cu_2(taec)Br(ClO_4)_3$ (type 2). The spectrum of $Cr_2(taec)Br_4$ was practically the same as that of the chloride. These results indicate that the present complexes have the type 1 structure. If so, the methylene groups on the 6- and 13-positions of the cyclam ring are located near the coordination sites of the metal centers, hindering the formation of six-coordination. In the case of $Cr_2(hmp)_4$,[9,10] the axial coordination sites are blocked by the methyl groups of the ligands. Hence, the high stability of this complex in air may partly be due to the steric configuration as observed for our complexes.

Acknowledgment. We wish to thank Prof. H. Ōkawa of Kyushu University for the magnetic susceptibility measurements and Prof. M. Mikuruya of Kwansei Gakuin University for his helpful advice and discussions. This work was partly supported by a Grant-in-Aid for Scientific Research (No. 62540478) from the Ministry of Education, Science and Culture.

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(15) Earnshow, A.; Larkworthy, L. F.; Patal, K. C. *J. Chem. Soc. A* **1969**, 1339.

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Spectroscopic Characterization of Cobalt(II)-Substituted *Achromobacter* Pseudoazurin: Similarity of the Metal Center in Co(II)-Pseudoazurin to Those in Co(II)-Plastocyanin and Co(II)-Plantacyanin

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Received April 27, 1988

Pseudoazurin is a bacterial blue copper protein, together with azurin, amicyanin, and rusticyanin.[2] There are three pseudoazurins so far isolated. Two proteins from denitrifying bacteria, *Achromobacter cycloclastes* IAM 1013[3,4] and *Alcaligenes faecalis* strain S-6[5] have one blue copper per 124[6] and 123[7] amino acid residues, respectively, being able to transfer electrons to their

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(2) Adman, E. T. In *Metalloproteins, Part 1: Topics in Molecular and Structural Biology*; Harrison, P. M., Ed.; MacMillan Press: London, 1985; pp 1–42.

(3) Iwasaki, H.; Matsubara, T. *J. Biochem.* **1973**, *73*, 659–661.

(4) Liu, M.-Y.; Liu, M.-C.; Payne, W. J.; Legall, J. *J. Bacteriol.* **1986**, *166*, 604–608.

(5) Kakutani, T.; Watanabe, H.; Arima, K.; Beppu, T. *J. Biochem.* **1981**, *89*, 463–472.

(6) Ambler, R. P. In *The Evolution of Metalloenzymes, Metalloproteins and Related Materials*; Leigh, G. J., Ed.; Symposium Press: London, 1977; pp 100–118.

(7) Hormel, S.; Adman, E. T.; Walsh, K. A.; Beppu, T.; Titani, K. *FEBS Lett.* **1986**, *197*, 301–304.