Pressure- and Temperature-Induced Valence Tautomeric Interconversion in a *o*-Dioxolene Adduct of a Cobalt – Tetraazamacrocycle Complex

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Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 60th birthday

Abstract: An electronic switch at the molecular level has been realized by using a class of ionic compounds of the formula [Co(L)(diox)]Y (L = tetraazamacrocyclic ligand, Y = mononegative anion). Such compounds undergo temperature- and pressure-induced intramolecular one-electron transfer equilibria. The transition temperature of interconversion varies with the nature of the counterions Y (Y = PF_6, BPh_4, I). Surprisingly the effect of the anion on the transition temperature is not only governed by its volume but also by its coulombic interaction.

Keywords: cobalt · electron transfer · isomerization · redox chemistry · valence isomerization

Introduction

Molecules that can be stable in at least two different forms are being investigated as possible candidates for information storage.[1, 2] Some dioxolene cobalt complexes of the formula $[Co(N\cap N)(diox)_2]$ ($N\cap N$ = diazine ligands, diox = *o*-dioxolene, that is catecholato (cat) or semiquinonato (sq)) have been recently shown to undergo valence-tautomeric equilibria between Co^{II} – semiquinonato and Co^{III} – catecholato species in the solid state, thus providing an interesting family of electronically labile derivatives.[3–8] The attractiveness of this class of complexes is that in principle the temperature of the transition between the two forms as well as the nature of the transition, namely continuous or abrupt, with or without hysteresis, can be tuned by molecular chemistry techniques, as already well estabilished for spin-crossover compounds.[9] To achieve this goal it is necessary to exploit all the possible experimental methods, including the possibility of varying the charge of the active species. We have found a class of ionic compounds of the formula [Co(L)(diox)]Y (L = tetraazamacrocyclic ligand, Y = mononegative anion) that undergoes temperature- and pressure-induced intramolecular one-electron transfer equilibria. Since the valence tautomers $[Co^{III}(L)(cat)]^+$ and $[Co^{II}(L)(sq)]^+$ are cationic, it is possible to tune the transition temperature of the interconversion by varying the nature of the counterions Y. As an example, we report here the synthesis and the physical properties of the [Co(cth)(phendiox)Y complexes] (cth = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; phendiox = 9,10-dioxophenanthrene; Y = PF_6, BPh_4, I).

Results and Discussion

The complex $[Co^{II}(cth)(phencat)]$ **(1)** (phencatH_2 = 9,10-dihydroxyphenanthrene) can be easily isolated from the reaction of $[Co(cth)Cl_2]$ and 9,10-dihydroxyphenanthrene in alkaline methanol under an inert atmosphere. The addition of a stoichiometric amount of $[Fe(Cp)_2]PF_6$ (Cp = C_5H_5) to a solution of **1** in methanol gives $[Co(CTH)(phendiox)]PF_6 \cdot H_2O$ (**2**), which can be recrystallized from dichloromethane/hexane as $[Co(cth)(phendiox)]PF_6 \cdot 1.5\,CH_2Cl_2$ (**3**).[10] The iodide and the tetraphenylborate derivatives, **4** and **5**, respectively, were prepared from the aerial oxidation of **1** followed by addition of aqueous KI, and from **2** by metathetic exchange with $NaBPh_4$ in methanol, respectively.

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Compound **2** is diamagnetic at low temperatures (Figure 1), but starting from about 150 K it becomes paramagnetic, and the χ_mT values increase with increasing temperatures, reaching the value of 2.55 emu K mol^{-1} ($\mu_{eff} = 4.34\,\mu_B$) at 340 K. The transition can be classified as gradual, in analogy with the definition currently used for spin-crossover complexes.[9] The phenomenon is associated with a color change from yellow at low temperatures to deep brown at high temperatures. On cooling the sample the yellow color is restored. No significant hysteresis effects were detected. This behavior is consistent with the existence of the valence-tautomeric equilibrium in Equation (1), which involves an intramolecular one-electron transfer process between the catecholato ligand and the low-spin cobalt(III) acceptor with a spontaneous change in spin state from Co^{III} ($S = 0$) to Co^{II} ($S = 3/2$) at the cobalt center. Spectral and structural evidence support this hypothesis (see below).

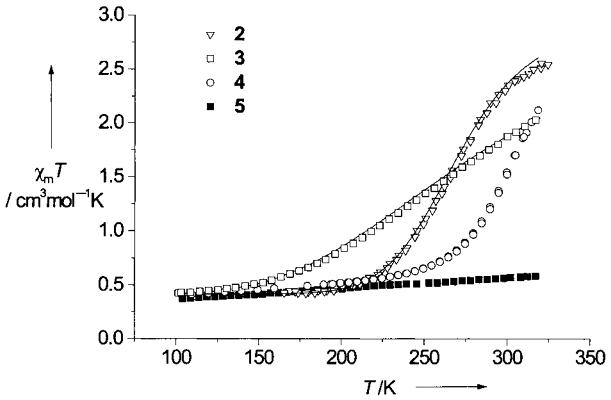

Figure 1. Plot of χ_mT versus T behavior of **2**–**5** in the range 100–340 K.

$$[\mathrm{Co^{III}(cth)(phencat)}]^+ \rightleftharpoons [\mathrm{Co^{II}(cth)(phensq)}]^+ \qquad (1)$$

The magnetic behavior of **3** is quite similar to that of **2** (Figure 1), although the χ_mT versus T function is much more gradual and still rising above room temperature, indicating that the valence-tautomeric interconversion in **3** extends to considerably higher temperatures than that in **2**. In addition, Figure 1 shows fits of the magnetic data by applying the regular solution model:[11] $\ln((1-x)/x) = (\Delta H + \Gamma(1-2x))/RT - \Delta S/R$, with the molar fractions $x = \chi_mT(\mathrm{obs}) - \chi_mT(\mathrm{LS}))/(\chi_mT(\mathrm{HS}) - \chi_mT(\mathrm{LS}))$, where $\chi_mT(\mathrm{LS})$ and $\chi_mT(\mathrm{HS})$ (LS = low spin, HS = high spin) have been taken as 0.4 (100 K) and 2.8 (saturation above 340 K). The entropy values ΔS (71.0 J mol^{-1} K^{-1} for **2**; 46.0 J mol^{-1} K^{-1} for **3**) and the enthalpy values ΔH (19.0 kJ mol^{-1} for **2**; 12.6 kJ mol^{-1} with a Gauss distribution width 2.7 kJ mol^{-1} for **3**) are definitely higher than for comparable iron(II) spin-crossover transition systems.[9] The excess of entropy reflects the change of the electronic structure not only at the metal center as in spin-crossover systems but in addition in the ligand. In compound **2** the long-range interaction parameter $\Gamma = 180\,\mathrm{cm}^{-1}$, while compound **3** shows practically no long-range interaction.

Temperature-dependent IR spectra of **2** confirm the existence of an equilibrium involving two species, as indicated by the presence of several isosbestic points in the range of 4000–500 cm^{-1}. The spectra in the range between 1750 and 1000 cm^{-1}, where some indicative bands associated with the C–O stretching and ring skeletal modes of the dioxolene ligands are expected,[12] are shown in Figure 2 and are consistent with a temperature-dependent change of the oxidation state of the coordinated dioxolene. At low temperatures the spectrum is consistent with the catecholato character of the dioxolene (bands in the range between 1330 and 1380 cm^{-1} associated with the C–O stretching mode), whereas at high temperatures a description as a semiquinonato species can be suggested (see for example the bands in the region between 1520 and 1590 cm^{-1}, which are assigned to the C=O stretching mode).

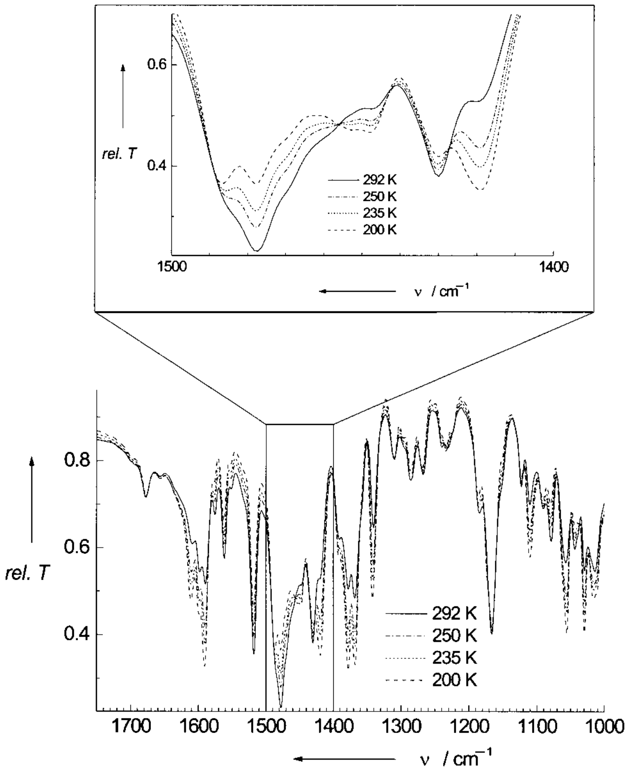

Figure 2. Temperature-dependent IR spectra of **2** in the range between 1750 and 1000 cm^{-1}. The insert shows several isosbestic points around 1400–1500 cm^{-1}.

The crystal structures of **3** at 295 and 198 K fully support the hypothesis of the valence-tautomeric interconversion. The space group was determined to be *C2/c* at 198 K and the refinement[13] showed that the same symmetry was present in an isomorphous cell at 295 K. At this temperature the dichloromethane molecules were found to be disordered. Since there is no change in the crystal symmetry, there is no crystallographic phase transition.

The strucutre of the cation at 198 K is shown as an ORTEP drawing in Figure 3. Selected bond lengths [Å] and angles [°] for **3** at 198 K and 295 K are collected in Table 1. The complex is six-coordinate; the macrocyclic ligand is ligated in a folded configuration and the dioxolene group acts as a bidentate ligand towards the metal ion. Comparing with the bond length

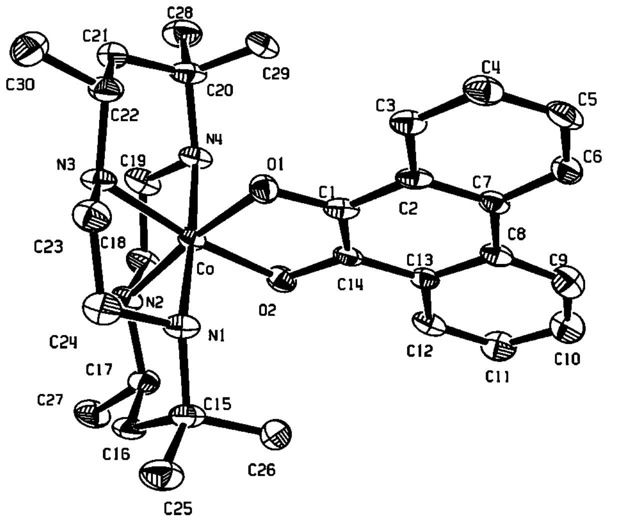

Figure 3. Structure of [Co(CTH)(phendiox)]$PF_6 \cdot 1.5CH_2Cl_2$ (**3**) at 198 K (ORTEP view; see Table 1 for selected bond lengths [Å] and angles [°] for **3** at 198 K and 295 K).

Table 1. Selected bond lengths [Å] and angles [°] for **3** at 198 K and 295 K.

	293 K	198 K
Co–O1	2.011(7)	1.887(4)
Co–O2	2.015(7)	1.911(4)
Co–N2	2.087(7)	2.011(5)
Co–N3	2.096(7)	2.030(5)
Co–N4	2.099(7)	2.014(5)
Co–N1	2.108(8)	2.022(5)
O1–C1	1.287(11)	1.368(7)
O2–C14	1.295(11)	1.352(7)
O1-Co-O2	81.5(3)	87.7(2)
O1-Co-N2	169.3(3)	173.4(2)
O2-Co-N2	90.4(3)	87.5(2)
O1-Co-N3	89.6(3)	86.5(2)
O2-Co-N3	169.2(3)	172.6(2)
N2-Co-N3	99.2(3)	98.7(2)
O1-Co-N4	102.1(3)	97.4(2)
O2-Co-N4	86.2(3)	85.2(2)
N2-Co-N4	84.1(3)	86.7(2)
N3-Co-N4	89.8(3)	91.0(2)
O1-Co-N1	84.5(3)	84.5(2)
O2-Co-N1	100.4(3)	96.9(2)
N2-Co-N1	90.2(3)	91.6(2)
N3-Co-N1	84.7(3)	87.1(2)
N4-Co-N1	171.3(3)	177.2(2)

data in the literature,[3, 14] at 198 K the features of the coordination polyhedron are consistent with an equilibrium mixture of the [Co^{III}(cth)(phencat)]$^+$ and [Co^{II}(cth)(phensq)]$^+$ valence tautomers; the first species is the dominant one at this temperature. The same conclusion can be drawn from the analysis of the structural parameters of the same cation at 295 K, with the difference that at this temperature the [Co^{II}(sq)] species is predominant, which is evident when the difference in the coordination sphere and C–O distances are compared for the two structures at the two temperatures (see data in Table 1). It is therefore concluded that the magnetic behavior of this compound is determined by a valence-tautomeric interconversion between the low-spin diamagnetic [Co^{III}(cat)] species and the high-spin [Co^{II}(sq)] one. The stereopacking diagram of this compound does not show the existence of strong interactions (such as hydrogen bonds and stacking interactions) between the neighboring complexes. These interactions would be important in the valence-tautomeric phase transition for inducing cooperativity within the crystal lattice. The observed packing can then justify the lack of any hysteresis effect in the valence-tautomeric transition.

As expected from the observation that the volume of the unit cell changes by 4.3 % on going from the [Co^{II}(sq)] species to the [Co^{III}(cat)] species, which is far more than can be accounted for by thermal contraction, it is clear that the magnetic properties of **2** must be pressure dependent (Figure 4). Indeed, the transition temperature increases with increasing pressure, thus indicating that the interconversion process can be isothermally pressure-induced. When the pressure reaches the value of 7.4 kbar, **2** is practically diamagnetic at room temperature. The observed result is in agreement with the physical behavior of some iron(II) and cobalt(II) spin-crossover complexes[9, 15] and of the [Co(phen)(dtbcat)(dtbsq)] complex (dtbcat = 3,5-di-*tert*-butylcatecholate, dtbsq = 3,5-di-*tert*-butylbenzosemiquinone) undergoing valence tautomerism.[16] In compound **2** the long-range interaction with $\Gamma = 180 \mathrm{cm}^{-1}$ at ambient pressure disappears at 3 kbar. The strong pressure dependence observed for **2** and the concomitant color change upon spin state change makes this valence-tautomeric system a potential canditate for a pressure sensor which should work after calibration at different temperatures.

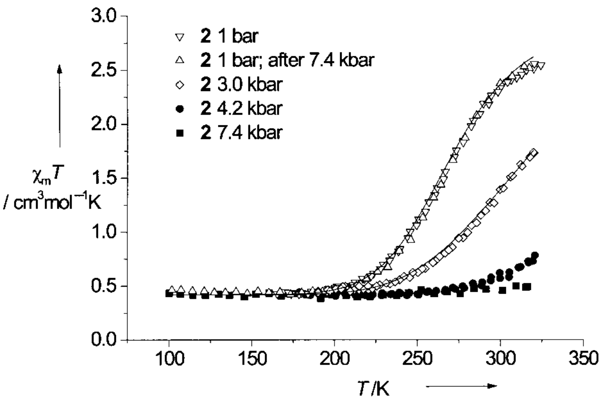

Figure 4. Pressure dependence of $\chi_m T$ versus T behavior of [Co(CTH)(phendiox)]$PF_6 \cdot H_2O$ (**2**). Measurements were done at ambient pressure (before and after release of pressure), 3.0, 4.2, and 7.4 kbar.

Figure 1 shows that the magnetic properties of the iodide derivative **4** are quite similar to that of **2**, the transition being shifted by about 30 K towards higher temperature, whereas those of the tetraphenylborate **5** are significantly different from those of the other compounds. The $\chi_m T$ versus T plot shows that compound **5** probably undergoes a similar transition but at much higher temperatures than the previous compounds. This shows how a different counterion, the tetraphenylborate, can deeply influence the intramolecular redox process. A similar result was recently observed for a manganese–dioxolene derivative.[17]

The high-temperature magnetic properties of the complexes reported herein are not easy to rationalize. However they could be consistent with the existence of a weak antiferromagnetic interaction between the cobalt(II) ion and the semiquinonate radical ligand, as recently established by some of us to be operative in some related octahedral cobalt(II)–semiquinonate complexes.[18] As observed for all the other cobalt systems undergoing valence-tautomeric equilibria,[19] no evidence of the formation of a low-spin Co^{II}–semiquinonato species was found. This species is expected to be characterized by a triplet electronic ground state, on the basis of the orthogonality of the d_σ(Co) and π^*(SQ) magnetic orbitals.[20] High-field ESR spectra did not show any evidence of the existence of such a species,[21] and this result is in full agreement with the observation of isosbestic points in the IR spectra of **2**, that is no more than two species are involved in the interconversion equilibrium. This result is in agreement with the results of quantum-mechanical calculations on this system,[22] and its possible explanation has been recently discussed.[23]

Conclusion

Temperature- and pressure-induced intramolecular one-electron transfer equilibria at the molecular level have been realized by using a class of ionic compounds of the formula [Co(cth)(phendiox)]Y complexes. The magnetic measurements reveal a rising paramagnetism with rising temperature indicating a transition. The temperature-dependent IR spectra show several isosbestic points, indicating the presence of two interconverting species: the catecholato (at low temperatures) and the semiquinonato (at high temperatures). The magnetic, structural, and the IR data therefore support the existence of the valence-tautomeric equilibrium given in Equation (1). The transition temperature of the interconversion varies with the nature of the counterions Y ($Y = PF_6$, BPh_4,I). Only the compound with the hydrated PF_6^- ion shows a long-range interaction ($\Gamma = 180\ cm^{-1}$). Application of pressure increases the transition temperature by stabilizing the Co^{III}(LS)–phencat state with a volume smaller than that of the Co^{II}(HS)-phensq state. The accompanying electron transfer alters the coulombic interaction between the anion Y and the Co^{III} center. On the other hand, variation of the anion Y is expected to cause chemical pressure: the transition temperature scales with the volume, as known from spin transitions[24], that is as seen by replacing PF_6 by I. On going from PF_6 to BPh_4, however, which is larger and is expected to lower the transition temperature, the opposite is observed. This can be understood on the grounds of the changing coulombic interaction. In the anion BPh_4 the electrons are less localized than those in PF_6. This alters the coulombic interaction, which stabilizes the Co^{III}(LS)–phencat state, and explains a rising transition temperature. Surprisingly, the effect of the anion on the transition temperature is not only governed by its volume but also by its coulombic interaction.

Experimental Section

Magnetic measurements: Magnetic susceptibility measurements at ambient pressure were performed with an applied field of 1 T on a Metronique SQUID operating between 2 and 280 K. Magnetic susceptibility measurements under hydrostatic pressure and variable-temperature were performed by using the PAR 151 Foner-type magnetometer, equipped with a cryostat operating in the temperature range 2–300 K. The hydrostatic pressure cell made of hardened beryllium bronze with silicon oil as the pressure transmitting medium operates in the pressure range of 1 bar $< P <$ 13 kbar and has been described elsewhere.[25a] Hydrostaticity was established in our previous studies of spin-crossover compounds.[25b–25d] The cylindrical sample holder is 1 mm in diameter and 5–7 mm in length. The pressure was measured by making use of the pressure dependence of the superconducting transition temperature of high purity tin as an internal standard. Experimental data were corrected for diamagnetism using Pascal's constants.

Middle infrared (MIR): MIR measurements were carried out on a Bruker IFS 66v/S FTIR-spectrometer equipped with an Oxford OptistatCF dynamic continuous flow helium cryostat with zinc selenide windows, which allowed measurements in a temperature range from 25 to 300 K. A globar light source was used. A DTGS detector was implemented for the MIR range and a KBr beam splitter was employed. The sample was mounted as a CsI pellet. The resolution of the spectra was set to 2 cm^{-1}, and 500 scans were accumulated for each spectrum.

Synthesis of [Co(CTH)(phendiox)]Y complexes ($Y = PF_6$, I, BPh_4): A solution of cobalt(II) acetate (3 mmol) in methanol (50 mL) was added to a solution of *dl*-CTH (3.3 mmol) under an inert atmosphere. The resulting solution was gently warmed for 0.5 h and then mixed with a solution of 9,10-di-hydroxyphenanthrene (3 mmol) in methanol (20 mL). After the addition of solid NaOH (6 mmol), the resulting mixture was gently warmed for 0.5 h and the volume of the resulting solution was reduced. Brown crystals of [Co(CTH)(Phencat)] (**1**) precipitated; yield 75%. They were filtered under argon, washed with ethanol–pentane mixtures, and then dried under an argon stream. A methanol solution of **1** (1 mmol) was mixed with a solution of ferricinium hexafluorophosphate (1 mmol) in acetone under an argon atmosphere. The volume of the resulting solution was reduced until crystals of $[Co(CTH)(phendiox)]PF_6 \cdot H_2O$ (**2**) appeared. They were filtered, washed with ethanol–pentane mixtures and dried under vacuum; yield 35%. Elemental analysis calcd (%) for $CoC_{30}F_6H_{46}N_4O_3P$ (**2**) (714.62): C 50.42, H 6.49, N 7.84, Co 8.25; found: C 50.30, H 6.59, N 7.72, C0 8.11. Recrystallization from dichloromethane–hexane mixtures afforded crystals of $[Co(CTH)(phendiox)]PF_6 \cdot 1.5\,CH_2Cl_2$ (**3**) that were filtered and dried under argon. Elemental analysis calcd (%) for $CoC_{31.5}Cl_3F_6H_{47}N_4O_2P$ (**3**) (824): C 45.92, H 5.75, N 6.80, Co 7.15; found: C 45.78, H 5.71, N 6.68, Co 7.04. Aerial oxidation of methanol solutions of **1** at room temperature (10 °C) followed by addition of aqueous solutions of potassium iodide and sodium tetraphenylborate gave [Co(CTH)(phendiox)]I (**4**) and $[Co(CTH)(Phendiox)]BPh_4$ (**5**), respectively, as microcrystalline powders; if sodium perchlorate is used unstable compounds were obtained. These compounds were recrystallized from methanol–water mixtures under an argon atmosphere, filtered, and dried under argon; following this process they were stable to air. Elemental analysis calcd (%) for $CoC_{30}\,H_{44}IN_4O_2$ (**4**) (678.54): C 53.08, H 6.54, N 8.26, Co 8.69; found: C 53.25, H 6.60, N 8.15, Co 8.52; elemental analysis calcd (%) for $CoBC_{54}H_{64}N_4O_2$ (**5**) (870.87): C 74.48, H 7.41, N 6.43, Co 6.77; found: C 74.22, H 7.31, N 6.27, Co 6.52.

Crystal data for 3

At 198 K: $CoCl_3C_{31.5}F_6N_4O_2P$, $M_r = 823.98$, crystal size $0.4 \times 0.6 \times 0.6$ mm, $Mo_{K\alpha}$ radiation 0.71069 Å, monoclinic space group *C*2/*c* (no. 15), $a = 20.289(4)$, $b = 12.305(3)$, $c = 29.189(8)$ Å, $\beta = 101.30(2)^\circ$, $V = 7146(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.532\ g\,cm^{-3}$, $\mu = 8.2\ cm^{-1}$. No decay was observed for 7342 reflections measured, 5470 independent reflections collected by ω scans ($5.06 < \theta < 48.4^\circ$) with $F^2 > 3\sigma(F^2)$; $R_1 = 0.067$, $wR_2 = 0.176$. The structure was solved by direct methods (SIR92[13a]) and refined by full-matrix least-squares on F^2 (SHELX93[13b]). All the non-hydrogen atoms were treated anisotropically. The hydrogen atoms were treated as fixed contributors in calculated positions with isotropic thermal parameters $B(H) = 1.2$ Beq. Disorder of the dichloromethane molecules was detected, which was modeled stepwise. Three different positions were included for one of the molecules, which were refined with complementary occupancy factors. The largest peak and hole in the final difference map were 1.017 and -1.118 eÅ^{-3}.

At 295 K (same crystal): $a = 20.291(2)$, $b = 12.649(1)$, $c = 29.681(3)$ Å, $\beta = 101.30(1)^\circ$, $V = 7470.3(12)$ Å^3, $\rho_{\text{calcd}} = 1.465$ g cm^{-3}, $\mu = 7.82$ cm^{-1}. For 4181 reflections measured by ω scans ($5.36 < \theta < 47.94^\circ$), 4052 independent reflections were collected with $F^2 > 3\sigma(F^2)$, $R_1 = 0.086$, $wR_2 = 0.239$. No decay was observed. Data were treated as previously described. Disorder of one of the dichloromethane molecules was detected but not treated. Largest peak and hole in the final difference map were 0.776 and -0.445 Å^{-3}. Selected bond lengths and angles at both $T = 198$ K and 295 K are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-103194 (295 K) and CCDC-103195 (198 K). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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