Preparation of Octabromoditechnetate(III,II), $[Tc_2Br_8]^{3-}$ and the Vibronic Structure of the $\delta \rightarrow \delta^*$ Transition

G. Peters, J. Skowronek, and W. Preetz
Institut für Anorganische Chemie der Christian-Albrechts-Universität, Kiel

Z. Naturforsch. **47a,** 591–594 (1992); received January 31, 1992

The dinstinct vibronic structure of the $\delta \rightarrow \delta^*$ transition of $Cs_3[Tc_2Br_8]$ with its mixed valence is well resolved at 6 K. The electronic origin at about 5970 cm^{-1} is split into four components, each giving rise to progressions entirely assignable in terms of $n\nu_1$ and $n\nu_1 + \nu_2$ up to $n = 9$, utilizing the totally symmetric stretching modes ν_1 (TcTc) and ν_2 (TcBr) exclusively.

Introduction

The mixed valence $[Tc_2Cl_8]^{3-}$ ion has been prepared prior to the discovery of the $[Tc_2Cl_8]^{2-}$ ion and the homologous octahalogenodirhenates $[Re_2X_8]^{2-}$, X = F, Cl, Br, I with eight metal electrons in each case forming a metal metal quadruple bond [1]. The $\sigma^2 \pi^4 \delta^2 \delta^*$ configuration of $[Tc_2Cl_8]^{3-}$ with one excess electron occupying the δ^* orbital leads to a Tc–Tc bond order of 3.5. For $K_3[Tc_2Cl_8] \cdot 2H_2O$ the spin- and orbitally-allowed $\delta \rightarrow \delta^*$ transition has been assigned in good agreement with SCF-X_α-SW calculations to a band originating in the near infrared region at 5900 cm^{-1} [2]. The vibrational progression on this transition is better resolved in the Cs-salt [3] and in the tetra(2-oxopyridinato)chloroditechnetate $Tc_2(OC_5H_4N)_4Cl$ [4]. The complicated vibronic structure of the latter compound has been assigned using polarized crystal spectra [4].

Altough a synthesis of $[Tc_2Br_8]^{3-}$ using pressurized hydrogen has been published [5], we have elaborated a more convenient route utilizing the reduction of $[Tc_2Br_8]^{2-}$ by $[BH_4]^-$ in organic solution [3]. In this paper the vibrational structure of the $\delta \rightarrow \delta^*$ transition measured at low temperature on $Cs_3[Tc_2Br_8]$ is reported.

Experimental

The route to $Cs_3[Tc_2Br_8]$

Commercially available NH_4TcO_4, sometimes black coloured due to self-reduction, is digested with NH_4OH/H_2O_2 until it is colourless, evaporated to dryness, dissolved in 0.1 n HNO_3 and precipitated as the *n*-tetrabutylammonium salt $(TBA)TcO_4$ by successive addition of $(TBA)HSO_4$. The precipitate is rinsed several times with ice cold water and dried over KOH at 10^{-3} Torr. Finely ground $(TBA)TcO_4$ is reacted repeatedly with several portions of concentrated HCl yielding 80–90% insoluble greyish-green $(TBA)[TcOCl_4]$. After drying it may be recrystallized from 1:3 (*v*/*v*) mixtures of dichloromethane/*n*-hexane or acetone/diethylether forming silvery-green flakes, or from hot saturated acetone or dichloromethane solutions on cooling to −30 °C.

Under stirring and a moderate argon-stream 1350 mg (2.7 mmol) $(TBA)[TcOCl_4]$ dissolved in tetrahydrofuran are mixed dropwise with 1400 mg (5.44 mmol) $(TBA)[BH_4]$ in 50 ml tetrahydrofuran forming a brown reaction mixture. To this diethylether is dropped until the entire brown intermediate is precipitated and the supernatant is colourless or transparent slightly yellow. After the supernatant is decanted the brown, sometimes oily residue is pumped for 24 hours at 10^{-3} Torr. The resulting brown powder is dissolved in 20 ml dichloromethane, and under admittance of air a stream of hydrogen chloride is passed through for about 15–20 minutes until the colour turns from brown to green or at least greenish-brown. The resulting solution is shaken under repeated exposure to air, admixed dropwise with diethylether until beginning turbidity and brought to crystallization of green $(TBA)_2[Tc_2Cl_8]$ at −30 °C. Yields depend strongly on the appropriate balance of the necessary exposure to air and amount up to 85%; excessive application of air increases formation of undesired yellow $(TBA)_2[TcCl_6]$, which can be recognized

---

Reprint requests to Prof. Dr. W. Preetz, Institut für Anorganische Chemie der Universität Kiel, Olshausenstraße 40, D-2300 Kiel.

0932-0784 / 92 / 0400-0591 $ 01.30/0. – Please order a reprint rather than making your own copy.

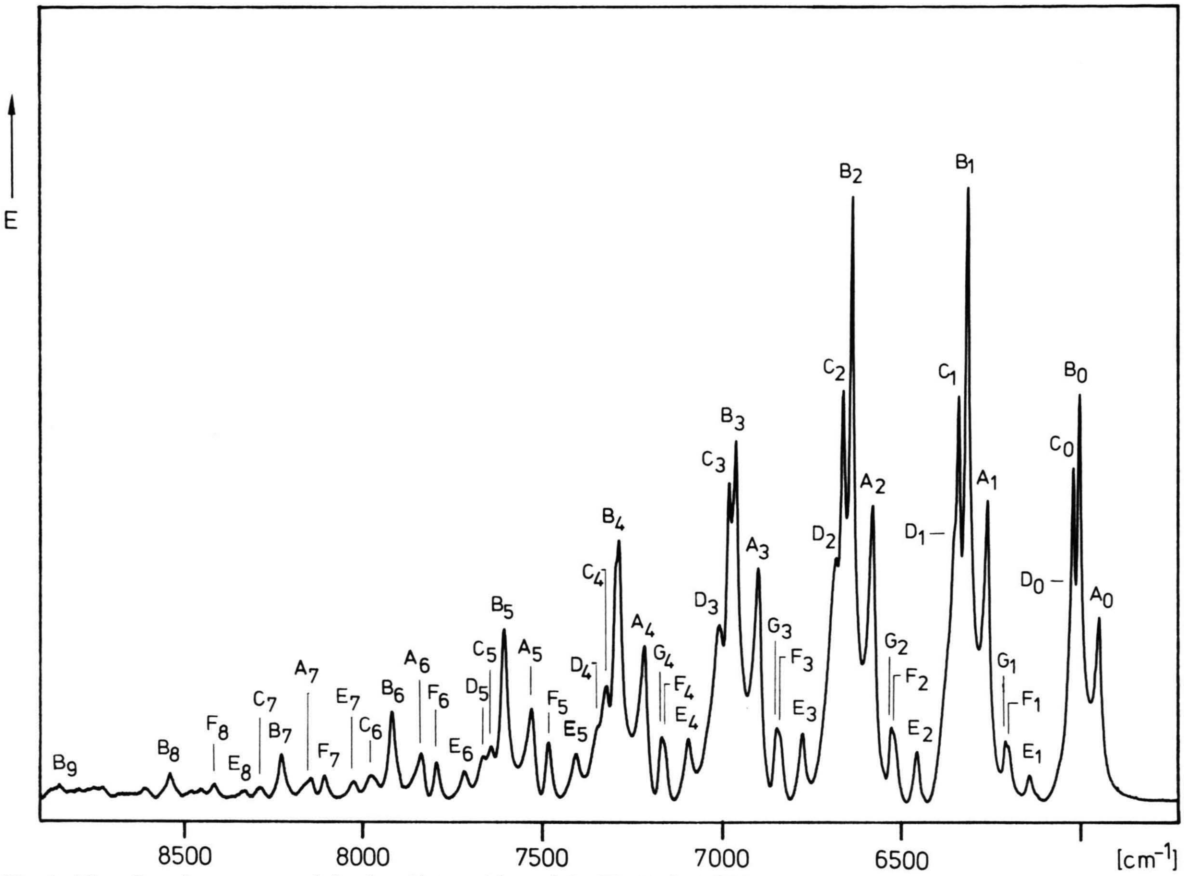

Fig. 1. The vibronic structure of the $\delta \rightarrow \delta^*$ transition of $Cs_3[Tc_2Br_8]$ at 6 K.

by its different colour and easily be removed by recrystallization from acetone or dichloromethane.

From $(TBA)_2[Tc_2Cl_8]$ by ligand exchange with bromine free hydrogen bromide in dichloromethane carmine red $(TBA)_2[Tc_2Br_8]$ is obtained quantitatively after evaporation and recrystallization from dichloromethane or acetone. Under rigorous exclusion of air equimolar amounts of $(TBA)_2[Tc_2Br_8]$ and $(TBA)[BH_4]$, both dissolved in a minimum of acetone, are admixed. From the discoloured solution upon cooling to $-30\,^\circ C$ golden $(TBA)_3[Tc_2Br_8]$ is formed in up to 70% yields. From a solution of $(TBA)_3[Tc_2Br_8]$ in constant boiling bromine free hydrobromic acid at room temperature $Cs_3[Tc_2Br_8]$ is precipitated nearly quantitatively on addition of CsBr.

Spectroscopy

The Raman data are collected on spinning samples at 80 K with a Jobin Yvon U 1000 from Instruments S.A., München, with use of argon and crypton laser excitation [6]. NIR spectra are recorded at room temperature and at 80 K on a spectrometer Acta M VII from Beckman, München, and at 6 K on a Fourier transform spectrometer IFS 113 v from Bruker, Karlsruhe, cooled by a KONTI-Kryostat Spectro A from Cryovac, Troisdorf. IR spectra are measured as CsBr discs with a Fourier transform spectrometer NIC 7199 from Nicolet Instruments GmbH, Offenbach/Main.

Results and Discussion

The well resolved vibrational progression of the band between 1100 and 2000 nm measured on powdered $Cs_3[Tc_2Br_8]$ in a CsBr disk at 6 K is shown in Figure 1. At room temperature we observe two hot bands at 1767 and 1874 nm as shown in Figure 2.

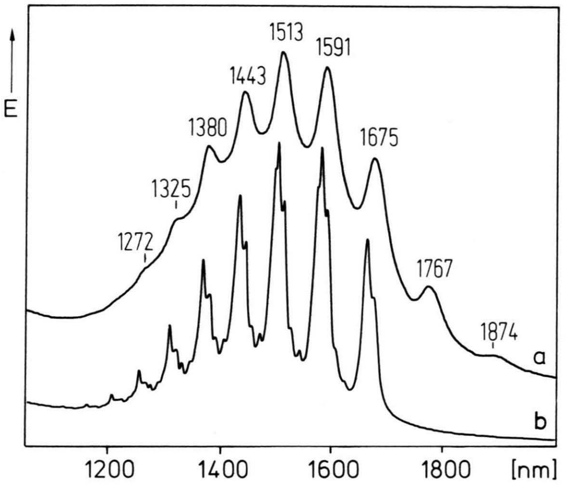

Fig. 2. The near infrared spectrum of $Cs_3[Tc_2Br_8]$ recorded at 295 K (a) and 77 K (b).

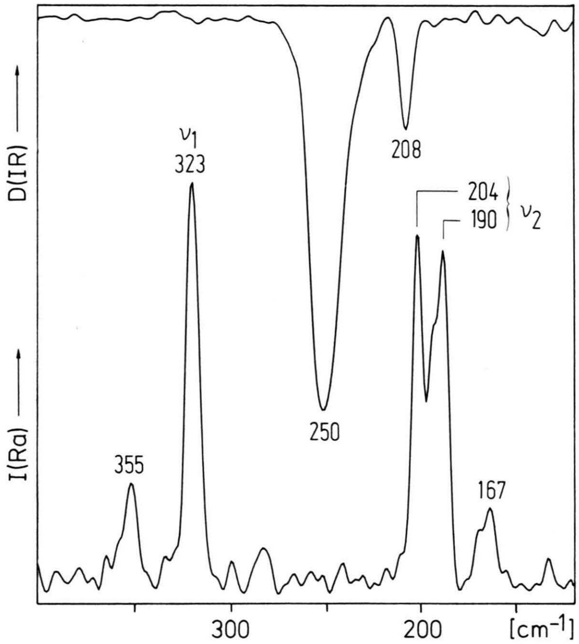

Fig. 3. Infrared (295 K) and Raman spectra (80 K, $\lambda_0 = 568.2$ nm) of $Cs_3[Tc_2Br_8]$.

They vanish completely at 77 K leaving the origin at about 5970 cm^{-1}, which is assigned to the $\delta \rightarrow \delta^*$ transition. The position and also the vibronic feature are very similar to the corresponding $\delta \rightarrow \delta^*$ transition of the homologous $[Tc_2Cl_8]^{3-}$ ion at 5900 cm^{-1} [2]. This insensitivity to halide substitution indicates the predominant metal-localized nature of the excita-

Table 1. Vibrational Structures of $Cs_3[Tc_2Br_8]$ in CsBr at 6 K.

Line	ν [cm^{-1}]	$\Delta\nu$[a] [cm^{-1}]	Intensity[b] [%]	Assignment
A_0	5948.8		32	A_0
B_0	6003.4		67	B_0
C_0	6019.2		55	C_0
D_0	6026.7[c]		38[d]	D_0
E_1	6138.8	190.0	6	$A_0 + \nu_2$
F_1	6199.1	195.7	11	$B_0 + \nu_2$
G_1	6206.4	187.2	12	$C_0 + \nu_2$
A_1	6261.2	312.4	50	$A_0 + \nu_1$
B_1	6318.1	314.7	100	$B_0 + \nu_1$
C_1	6344.1	324.9	66	$C_0 + \nu_1$
D_1	6353.7	327.0	45	$D_0 + \nu_1$
E_2	6456.6	507.8	10	$A_0 + \nu_1 + \nu_2$
F_2	6518.4	515.0	13	$B_0 + \nu_1 + \nu_2$
G_2	6528.3	509.1	14	$C_0 + \nu_1 + \nu_2$
A_2	6581.5	632.7	50	$A_0 + 2\nu_1$
B_2	6640.2	636.8	98	$B_0 + 2\nu_1$
C_2	6666.6	647.4	68	$C_0 + 2\nu_1$
D_2	6684.4	657.7	41	$D_0 + 2\nu_1$
E_3	6778.7	829.9	13	$A_0 + 2\nu_1 + \nu_2$
F_3	6842.9	839.5	13	$B_0 + 2\nu_1 + \nu_2$
G_3	6850.7	831.5	14	$C_0 + 2\nu_1 + \nu_2$
A_3	6902.8	954.0	39	$A_0 + 3\nu_1$
B_3	6966.4	963.0	66	$B_0 + 3\nu_1$
C_3	6985.4	966.2	53	$C_0 + 3\nu_1$
D_3	7011.1	984.4	30	$D_0 + 3\nu_1$
E_4	7094.7	1145.9	12	$A_0 + 3\nu_1 + \nu_2$
F_4	7162.1	1158.7	12	$B_0 + 3\nu_1 + \nu_2$
G_4	7168.8	1149.6	12	$C_0 + 3\nu_1 + \nu_2$
A_4	7220.4	1271.6	27	$A_0 + 4\nu_1$
B_4	7290.9	1287.5	43	$B_0 + 4\nu_1$
C_4	7325.3	1306.1	20	$C_0 + 4\nu_1$
D_4	7348.3	1321.6	14	$D_0 + 4\nu_1$
E_5	7409.1	1460.3	10	$A_0 + 4\nu_1 + \nu_2$
F_5	7485.0	1481.6	11	$B_0 + 4\nu_1 + \nu_2$
		(1465.8)		$(C_0 + 4\nu_1 + \nu_2)$
A_5	7533.4	1584.6	17	$A_0 + 5\nu_1$
B_5	7611.4	1608.0	29	$B_0 + 5\nu_1$
C_5	7646.9	1627.7	11	$C_0 + 5\nu_1$
D_5	7669.6	1642.9	9	$D_0 + 5\nu_1$
E_6	7722.7	1773.9	7	$A_0 + 5\nu_1 + \nu_2$
F_6	7801.7	1798.3	8	$B_0 + 5\nu_1 + \nu_2$
		(1782.5)		$(C_0 + 5\nu_1 + \nu_2)$
A_6	7845.1	1896.3	10	$A_0 + 6\nu_1$
B_6	7926.5	1923.1	13	$B_0 + 6\nu_1$
C_6	7981.9	1962.7	6	$C_0 + 6\nu_1$
E_7	8031.5	2082.7	5	$A_0 + 6\nu_1 + \nu_2$
F_7	8113.9	2110.5	6	$B_0 + 6\nu_1 + \nu_2$
		(2094.7)		$(C_0 + 6\nu_1 + \nu_2)$
A_7	8153.0	2204.2	6	$A_0 + 7\nu_1$
B_7	8238.4	2235.0	9	$B_0 + 7\nu_1$
C_7	8298.0	2278.8	4	$C_0 + 7\nu_1$
E_8	8343.2	2394.4	4	$A_0 + 7\nu_1 + \nu_2$
F_8	8425.8	2422.4	5	$B_0 + 7\nu_1 + \nu_2$
		(2406.6)		$(C_0 + 7\nu_1 + \nu_2)$
A_8	8462.3	2513.5	4	$A_0 + 8\nu_1$
B_8	8548.8	2545.4	6	$B_0 + 8\nu_1$
C_8	8618.4	2599.2	4	$C_0 + 8\nu_1$
A_9	8805.8	2857.0	4	$A_0 + 9\nu_1$
B_9	8859.1	2855.7	4	$B_0 + 9\nu_1$
C_9	8944.2	2925.0	4	$C_0 + 9\nu_1$

[a] Differences from the corresponding origin A_0, B_0, C_0, or D_0.

[b] Intensity corresponding to $B_1 = 100\%$.

[c] Calculated from differences to C_0.

[d] Estimated intensity.

Table 2. Average Values of ν_1 and ν_2 in the Excited State.

Progression	Origin	Vibration	Average value standard deviation [cm^{-1}]/[cm^{-1}]	Number of considered vibrational progressions
A	A_0	ν_1	316.0/1.9	9
B	B_0	ν_1	319.1/2.4	9
C	C_0	ν_1	324.9/1.5	9
D	D_0	ν_1	328.6/1.2	5
E	A_0	ν_2	194.5/3.2	6
F	B_0	ν_2	198.6/3.2	4
G	C_0	ν_2	182.0/5.2	4

tion. The energy differences between the O–O-transition and the first and second hot band are 311 and 634 cm^{-1}, respectively, corresponding to the ground state frequency of 323 cm^{-1}. The origin is split into four transitions A_0, B_0, C_0 and D_0 lying closely together (Table 1). There are several possible explanations for the multiple character of the O–O transition, e. g. Davydoff splitting, nonequivalence of disordered $[Tc_2Br_8]^{3-}$ units, site differences or partial loss of solvent molecules, probably water, in the crystal environment. The latter is emphasized by varying intensities of the totally symmetric Tc–Tc and Tc–Br stretching vibrations ν_1 at 323 cm^{-1} and ν_2 at 204 and 190 cm^{-1} upon prolonged exposure of the compound to vacuum (Figure 3).

Despite the complexity of the vibrational structure we approached a general assignment using only progressions of the totally symmetric vibrations ν_1 and ν_2. In Table 1 the observed frequencies, intensities and assignments are listed. The most remarkable feature of the spectrum are the intense progressions with up to 9 ν_1 built on the different components of the O–O transition. A second progression derived from combination tones of the type $n\,\nu_1 + \nu_2$ with only 10–20% intensity of the first one is detectable, despite their weakness, up to $n = 7$. In dependence on the O–O origin different frequencies for ν_1 in the excited state are deduced, Table 2. The lowest average value calculated from coupling to A_0 is 316.0 cm^{-1}, the highest is 328.6 cm^{-1} from coupling to D_0. The decrease of ν_1 from the ground state to the excited state for the *A* and *B* progressions in the order of 1 to 2% is reasonable and consistent with the decrease of bond order by promoting one electron from the weakly bonding δ to the weakly antibonding δ^* orbital. The average frequencies of ν_1 in the excited state derived from the *C* and *D* series seem to be about 0.6 and 1.7% greater than in the ground state. This appearance is explained by weak ν_1 components with accordingly higher frequencies, unobservable in the Raman spectrum. Whereas the intensity distribution patterns in the *A* and *B* series, as indicated by their Franck-Condon factors of 0.09 and 0.10 are similar to each other, the *C* and *D* progressions represent another group of vibrational structure with Franck-Condon factors of 0.14 and 0.13. Therefore it seems likely that the two groups of vibrational structures, represented by the *A*, *B*, and *C*, *D* series, respectively, indicate a larger crystal field splitting between the two series than within them.

Since the combination tones $n\,\nu_1 + \nu_2$ are less intensive than the major progressions with ν_1, the $n\,\nu_1 + \nu_2$ couplings to B_0 and C_0 for $n > 4$, are not resolved, preventing an unambiguous assignment. A progression of $\nu_1 + \nu_2$ based on D_0 is not observable, either due to its low intensity or to interference with C_0 absorptions. The values of ν_2 in the excited state calculated from the *E*, *F*, and *G* series are also dependening on the origin, Table 2. The energy difference of 16.6 cm^{-1} derived from the *G* (182.0 cm^{-1}) and the *F* (198.6 cm^{-1}) progressions corresponds to the 14 cm^{-1} splitting of the ground state stretching frequency of ν_2 (204 and 190 cm^{-1}, vide Figure 2).

Acknowledgement

We thank the "Deutsche Forschungsgemeinschaft" and the "Fonds der Chemischen Industrie" for support and we are grateful to Professor H. H. Schmidtke and Dr. H. J. Mink, Universität Düsseldorf, for measuring the 6 K spectrum.

[1] F. A. Cotton and R. A. Walton, Multiple Bonds Between Metal Atoms, Wiley-Interscience, New York 1982.

[2] F. A. Cotton, P. E. Fanwick, L. D. Gage, B. Kalbacher, and D. S. Martin, J. Amer. Chem. Soc. **99**, 5642 (1977).

[3] G. Peters, Dissertation, Kiel 1982.

[4] F. A. Cotton, P. E. Fanwick, and L. D. Gage, J. Amer. Chem. Soc. **102**, 1570 (1980).

[5] V. I. Spitsyn, A. F. Kuzina, A. A. Oblova, and S. V. Kryuchkov, Russ. Chem. Rev. **54**, 373 (1985).

[6] H. Homborg and W. Preetz, Spectrochim. Acta **32a**, 709 (1976).