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Infrared and Raman Spectra of Magnus' Green Salt, $[Pt(NH_3)_4][PtCl_4]$, and Its Deuterate

J. R. HALL and D. A. HIRONS

Department of Chemistry, University of Queensland, Brisbane, Qld., Australia 4067

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Evidence has now been obtained to confirm an earlier assignment [1] made for a band, whose origin was uncertain, in the far infrared spectrum of Magnus' Green Salt, $[Pt(NH_3)_4][PtCl_4]$. The particular feature, occurring at *ca.* 200 cm^{-1}, increased markedly in intensity when the temperature of the sample was lowered from ambient to liquid nitrogen temperature. Initially the band was assigned [2] to the A_{2u} translational lattice mode involving the chain of Pt atoms in the columnar array of cations and anions [3]. The frequency of 200 cm^{-1} was considered too high for this mode and it was reassigned to NH_3 torsional motion [1].

Confirmation of this assignment has been achieved by recording the far infrared spectrum of the deuterated salt. The Raman spectrum of the deuterate has also been obtained.

Results and Discussion

The Table lists infrared and Raman frequencies for microcrystalline $[Pt(NH_3)_4][PtCl_4]$ and the

TABLE I. Infrared and Raman Spectra (cm^{-1}) of MGS and Its Deuterate.

$[Pt(NH_3)_4][PtCl_4]$			Assignments	$[Pt(ND_3)_4][PtCl_4]$		
IR		R		IR		R
R.T.	77 K	R.T.		R.T.	77 K	R.T.
72s	75s		lattice mode	72s	74s	
84w	90w		lattice mode	84w	89w	
143m	144m		π(Pt–Cl)	144m[a]	144w	
			τND_3		158s	
170w	172w		δ(Pt–Cl)	170w	170w	
		175m	δ(Pt–Cl)			173m
200w, br	212s		τNH_3			
242s	248s		π(Pt–N)	208vs	208vs	
263s	266s		δ(Pt–N)	236m	238s	
		267w	δ(Pt–N)			245w
	294w			292sh	293w	
		297w				300w
304sh	307sh		ν(Pt–Cl)	305sh	305sh	
310vs	313vs			308vs	310vs	
		316s				318s
502vw				461w		
		521vw	ν(Pt–N)			480vw
		537m				499m
827vs						
845sh			ρNH_3	636vs		
1305 vs				1012vs		
1312						1100mbr
		1322w				
1547m			δNH_3	1073 w		
1580w				1086		
1632s				1151s		
1662w						
1695w						
3190s		3220w		2310s		2340w
3280vs		3280w	ν(N–H)	2440vs		2450w
3450w						

[a] Indicates intensity from the unresolved torsional mode.

deuterated salt. The spectra of the hydrogen compound agree with the far infrared spectrum reported by Hiraishi *et al.* [2] and the low-range single crystal spectra [1]. Wide-range spectra have not been reported previously.

Skeletal Region

A comparison of the far infrared spectra of MGS and its deuterate (see Fig. 1) clearly distinguishes between the cation and anion contributions. Features at 313, 307 and 294 cm^{-1} (Pt–Cl stretching) and 172 and 144 cm^{-1} (Pt–Cl bending) are unaffected by deuteration (the corresponding lines in the Raman spectrum of MGS are likewise unaffected). On the other hand those bands attributed to Pt–N deformation modes decrease by 20–40 cm^{-1} on deuteration. These shifts correspond to the effect of deuteration on the infrared spectrum of the analogous species $Cu(NH_3)_4^{2+}$ [4]. In this case the infrared active modes shift by 10–20 cm^{-1}. The Raman active in-plane Pt–N deformation modes of MGS decrease from 267 to 245 cm^{-1}. The corresponding mode in the Raman spectrum of $[Pt(NH_3)_4]Cl_2$ shifts by 32 cm^{-1} [5]. The Pt–N stretching modes decrease appropriately on deuteration *viz.*, from 502 to 461 cm^{-1}(ir) and 537 and 520 cm^{-1} to 499 and 480 cm^{-1} (Raman). The lattice modes are unchanged.

The most significant shift on deuteration occurs with the 200 cm^{-1} band. This would not be noticeably influenced by deuteration if it were due to Pt–Pt–Pt stretching [2]. The shift from 212 cm^{-1} to 158 cm^{-1} corresponds to ν_H/ν_D = 1.34, thus confirming its assignment to NH_3 torsional motion [1]. Hiraishi *et al.* report temperature sensitive features around 200 cm^{-1} in the far infrared spectra of $[Pd(NH_3)_4][PdCl_4]$, $[Pt(NH_3)_4][PtBr_4]$ and $[Pd(NH_3)_4][PdBr_4]$. The assignment of the band to NH_3 torsional motion appears appropriate in these cases also.

Ligand Modes

The assignment of the NH_3 modes is straightforward. Bands occurring in the range 3190–3450 cm^{-1} are assigned to N–H stretching. These shift to 2310–2450 cm^{-1} on deuteration. The NH_3 deformation modes range in frequency from 1305 (symmetric type) to 1695 cm^{-1} (antisymmetric type) and the corresponding modes for ND_3 have frequencies of 1012 cm^{-1} and 1073–1151 cm^{-1}. The Raman active deformation mode shifts from 1322 to 1100 cm^{-1}. The intense, infrared active rocking mode at 827 cm^{-1} shifts to 636 cm^{-1} on deuteration.

The spectra of deuterated MGS completely vindicate the assignments made for the hydrogen form.

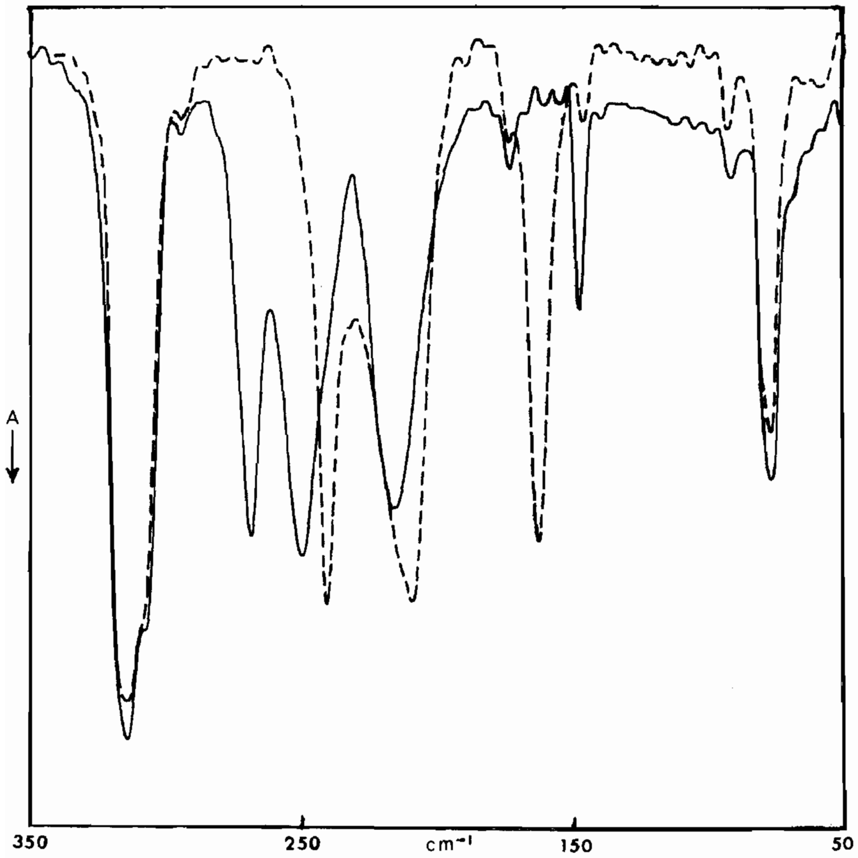

Fig. 1. Ratioed spectra (77 K) of $[Pt(NH_3)_4][PtCl_4]$ (——) and its deuterate (– – –).

Experimental

MGS was prepared according to the method of Keller [6] $[Pt(ND_3)_4][PtCl_4]$ was prepared by adding together stoichiometric quantities of D_2O solutions of K_2PtCl_4 and $[Pt(ND_3)_4]Cl_2 \cdot D_2O$. The latter compound was obtained by dissolving $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ in D_2O and evaporating to dryness. This procedure was carried out three times.

Infrared spectra were recorded using Perkin-Elmer Model 225 (4000–200 cm^{-1}) and Beckmann-RIIC IR-720 (400–50 cm^{-1}) spectrophotometers. Samples were examined as Nujol and hexachlorobutadiene mulls at room temperature. Spectra at 77 K were obtained using an Oxford Instrument Co. Ltd (Model CF100) cryostat.

Raman spectra were recorded using a Cary 82 spectrometer and both 515 and 488 nm radiation. A rotating cell containing compressed MGS yielded slightly better spectra than a capillary containing a microcrystalline sample but the 3200 cm^{-1} region was complicated by the presence of non-lasing discharge lines of the Ar^+ laser. The deuterate was examined in a capillary tube only. Capillary-held samples were decomposed by >40 mW of laser power. Spectral slit widths down to 3 cm^{-1} were used. Infrared and Raman frequencies are considered accurate to ± 2 cm^{-1} below 2000 cm^{-1} and ± 4 cm^{-1} above 2000 cm^{-1}.

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