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Constraint and Electronegativity Effects on ^{77}Se–^{31}P Spin–Spin Couplings in Selenophosphoryl Compounds

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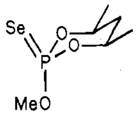
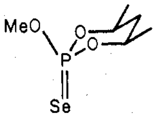
Four new constrained selenophosphates (**1**–**4**) are reported and the trend of increasing $J_{\text{Se–P}}$ upon constraint is discussed. These couplings are also reported for a new constrained triaminophosphine selenide (**5**) and for three cage tris(hydrazino)diphosphine selenides (**6**–**8**). The ratio of chair conformers in $MeO(Se)POCH_2CH_2CH_2O$ (**9**) is also calculated via a consideration of $J_{\text{Se–P}}$ couplings. Expressions for linear correlations of $J_{\text{Se–P}}$ with the average electronegativity of the phosphorus substituent in acyclic selenophosphoryl compounds are given.

Owing primarily to the advent of FT instrumentation, one-bond Se–P couplings (as well as $\delta(^{77}Se)$ and $\delta(^{31}P)$ chemical shifts) have been recorded[1–21] for nearly 100 selenophosphoryl ($Se{=}PZ_3$) compounds since 1971 when the first such coupling was reported.[22] The large range of $J_{\text{Se–P}}$ values ($\sim$475 Hz[7,9]) provides a sensitive probe of the inductive effect of the phosphorus substituents.[1,3,5,8] These couplings are also useful for assigning structures of isomers involving the selenium–phosphorus bond (e.g., $SeP(OEt)_3$ vs. $OP(OEt)_2SeEt$ and axial vs. equatorial Se in $MeO(Se)POCH_2CH_2CH\text{-}MeO$)[1,10,11,13–16,20–22] and of reaction products of selenophosphorus compounds with halogens.[23a] The sign of the reduced coupling constant $K_{\text{Se–P}}$ has been determined to be negative in both Se=P and Se–P systems.[2,3,18,22] This observation has been interpreted[7] to arise from the dominance of the negative core s electron polarization term[23b,c] over the positive direct Fermi contact term[23b,c] for selenium while the reverse is true for pentavalent phosphorus.

In this paper we report the synthesis of the constrained selenophosphoryl compounds **1**–**5**. The $J_{\text{Se–P}}$ couplings obtained for these compounds and **6**–**8** are rationalized in terms of rising effective electronegativity of the phosphorus substituents upon constraint into ring and cage structures. A substantially higher coupling value has been obtained for **2** than that previously reported.[19] Our value permits the realization of good linear correlations of P=Se couplings in a variety of selenophosphates, with NMR and IR data on related systems. The constant for the equilibrium


1a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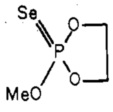
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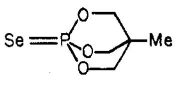
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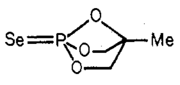
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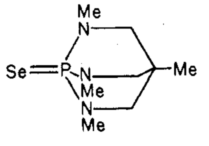
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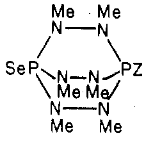
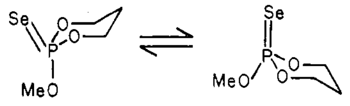

6, Z = NPh[24]
7, Z = Se[25]
8, Z = O[24]


9a **9b**

is calculated from its Se–P coupling employing the coupling data from the rigid isomers **1a** and **1b**. Excellent linear correlations of $J_{\text{Se–P}}$ values with the average electronegativity of the phosphorus substituents are also demonstrated with literature data on acyclic selenophosphoryl compounds.

Experimental Section

^{31}P NMR spectra were obtained on solutions in 10-mm tubes with a Bruker HX-90 instrument operating at 36.434 MHz in the FT mode. The spectrometer was locked on the ^{2}H resonance of the deuterated solvent. The external standard was 85% H_3PO_4 contained in a 1-mm capillary held coaxially in the sample tube by a PTFE vortex plug. Positive shifts are those downfield of the standard.

Mass spectra were obtained on an AEI MS902 high-resolution spectrometer or on a Finnigan 4000 instrument.

Red selenium,[26] KSeCN,[27] $SeP(NMe_2)_3$,[28] $SeP(OMe)_3$,[29] **6**,[24] **7**,[25] **8**,[24] and the trivalent phosphorus precursors to **1**,[30] **2**,[31] **3**,[32] **4**,[33] and **9**[31] were prepared as reported elsewhere.

$P(NMeCH_2)_3CMe$ (2). Although the preparation of this compound has been reported previously,[34,35] the modifications described below lead to a significantly better yield of one of the intermediates. The tribromide prepared earlier[35] was converted to the final intermediate $CH_3C(CH_2NHMe)_3$ in 96% yield (compared to 80[34] and 22%[35]) by dissolving 93.0 g (0.301 mol) in 300 mL of ethanol in a flask fitted with a dry-ice condenser. After the mixture was cooled in an ice bath, 150 mL of $MeNH_2$ was condensed into the solution and the solution transferred into a 500-mL Teflon-lined pressure reactor. The reactor was heated to 190 °C for 24 h with vigorous stirring after which it was allowed to cool to room temperature. Evaporation of excess $MeNH_2$ and removal of the ethanol on a rotary evaporator left a white solid to which was added 400 mL of benzene. The mixture was refluxed under a nitrogen atmosphere for a 9-h period, during the first hour of which was added 100 g of 86% assay KOH. After the mixture was cooled to room temperature and after filtration and removal of the solvent on a rotary evaporator, the yellow oil was distilled (bp 72 °C) to give 46.0 g of the pure triamine.

$MeO(Se)POCHMeCH_2CHMeO$ (1a and 1b). A mixture of 2.00 g (12.2 mmol) of the precursor phosphite (axial OMe isomer) to **1a** and 1.60 g (20.3 mg-atoms) of red selenium in 15 mL of toluene was heated to 80 °C for 18 h. The hot mixture was filtered and cooled to room temperature, and the solvent was removed under vacuum. The residue was recrystallized from *n*-hexane at −78 °C to give 2.46 g (83%) of **1a** (mp 68–70 °C; *m/e* for P^+ 243.1019 ± 0.0016, calcd 243.1025).

A mixture of 1.05 g (7.31 mmol) of KSeCN and 1.19 g (7.23 mmol) of the cyclic phosphite precursor (equatorial OMe isomer) to **1b** in 25 mL of dry acetonitrile was stirred at room temperature for 90 min under a N_2 atmosphere. The acetonitrile was evaporated in vacuo and the remaining white mass was extracted with 20 mL of dry benzene and filtered under a N_2 atmosphere. Evaporation of the

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Table I. ^{31}P NMR Chemical Shifts and $J_{\mathrm{Se-P}}$ Coupling Constants[a]

	$\delta(^{31}\mathrm{P})$, ±0.1 ppm	$J_{\mathrm{Se-P}}$, ±1 Hz		$\delta(^{31}\mathrm{P})$, ±0.1 ppm	$J_{\mathrm{Se-P}}$, ±1 Hz
$\mathrm{SeP(OMe)_3}$	78.0	954	$\mathrm{SeP(NMe_2)_3}$	82.5	784
1a	66.8	996	**5**	77.7	854
1b	68.8	949	**6**	67.0[c], 7.3[d]	918
2	88.0	1011[b]	**7**	66.2	923
3	60.1	1053	**8**	67.3[c], 8.0[e]	926
4	81.4	1099	**9**	68.6	985[f]

[a] In $\mathrm{CDCl_3}$ solution at 23 °C. All reduced couplings K are undoubtedly negative (see text). [b] 948 Hz was reported earlier;[19] see text. [c] Se=P. [d] P=NPh. [e] P=O. [f] 968 Hz was reported earlier.[19]

filtrate in vacuo yielded the crude liquid product.[36] Due to the tendency for rearrangement to the more stable isomer (axial OMe), no attempt was made to distill the product. Purity, as judged from ^{31}P NMR, was better than 80%.

$\mathrm{MeO(Se)\overline{POCH_2CH_2O}}$ (2). A mixture of 2.51 g (20.6 mmol) of the cyclic phosphite and 3.01 g (20.9 mmol) of KSeCN in 25 mL of dry acetonitrile was stirred at room temperature for 2 h under a $\mathrm{N_2}$ atmosphere. The acetonitrile was evaporated in vacuo and the white residue extracted with 20 mL of dry benzene and filtered under $\mathrm{N_2}$. Evaporation of the benzene in vacuo yielded the crude product which solidified on standing.[36] Attempts at purification of the crude material, including chromatography, resulted in decomposition, and the unpurified material was used for the determination of $^1J_{\mathrm{P-Se}}$. Purity, as judged from the ^{31}P spectrum, was approximately 78%, and a mass spectrum confirmed the identity of the material (see Results and Discussion).

$\mathrm{SeP(OCH_2)_3CMe}$ (3). A mixture of 4.74 g (32.0 mmol) of freshly sublimed caged phosphite and 3.80 g (47.0 mg-atoms) of red selenium in 25 mL of toluene was heated at 80 °C for 10 h. The hot mixture was filtered, and the solid residue was extracted with 150 mL of toluene in a Soxhlet apparatus for 2 days under nitrogen. The solid which precipitated upon cooling to room temperature was recrystallized from 300 mL of boiling toluene, washed with two 30-mL portions of hexane, and dried in vacuo to give 6.36 g (88%) of white product (mp 246–248 °C; m/e for P$^+$ 227.9454 ± 0.0014, calcd 227.9454).

$\mathrm{Se\overline{P(OCH_2)_2CO}Me}$ (4). A mixture of 0.60 mL (5.8 mmol) of caged phosphite and 0.86 g (11 mg atoms) of red selenium in 15 mL of toluene was heated at 75 °C for 10 h. The mixture was then cooled to room temperature and filtered. The filtrate was further cooled to −78 °C and the product crystallized to give 0.78 g (63%) of white solid. This compound is very unstable to atmospheric moisture and also decomposed slowly at room temperature under nitrogen, both processes giving red selenium as a product (mp 74–76 °C; m/e for P$^+$ 213.9289 ± 0.0014, calcd 213.9297).

$\mathrm{SeP(NMeCH_2)_3CMe}$ (5). A mixture of 1.00 mL (5.60 mmol) of caged triaminophosphine and 0.94 g (12 mg-atoms) of red selenium in 30 mL of benzene was heated at 70 °C for 10 h. The mixture was cooled to room temperature and filtered, and the solvent was removed under vacuum. The remaining solid was sublimed at 60 °C at 0.01 torr to give 1.14 g (77%) of product (mp 118–120 °C; m/e for P$^+$ 267.0404 ± 0.0017, calcd 267.0403).

$\mathrm{MeO(Se)\overline{POCH_2CH_2CH_2O}}$ (9). A mixture of 1.34 g (9.84 mmol) of the cyclic phosphite precursor and 1.42 g (9.86 mmol) of KSeCN in 25 mL of dry acetonitrile was stirred at room temperature for 2 h under a $\mathrm{N_2}$ atmosphere. The acetonitrile was evaporated in vacuo and the white residue extracted with 20 mL of dry benzene and filtered under $\mathrm{N_2}$. The benzene was removed from the filtrate in vacuo, affording the crude liquid product.[36] No attempt was made to distill the product due to the Pishschimuka rearrangement previously reported[19] to occur upon distillation.

Results and Discussion

$J_{\mathrm{Se-P}}$ and Constraint. The $J_{\mathrm{Se-P}}$ couplings in excess of 1000 Hz listed in Table I for selenophosphates **2–4** are considerably larger than those reported previously for acyclic $\mathrm{SeP(OR)_3}$ compounds (935–952 Hz[1-3,7]). It is also apparent from our data that the progression in this coupling follows the order **1b** < $\mathrm{SeP(OMe)_3}$ < **1a** < **2** < **3** < **4** which is also that found for the trend in B–H stretching frequencies of the borane adducts of the phosphites[33] (i.e., $\mathrm{H_3B}$ in place of Se in **1–4**). Plots of $J_{\mathrm{Se-P}}$ vs. ν(BH(asym)) and ν(BH(sym)) and the weighted average of these values are reasonably linear as shown by eq 1–3.

Table II. Linear Correlation Data on $J_{\mathrm{Se-P}}$ vs. Substituent Electronegativity[a]

equation	correl coeff	electronegativity scale	ref
$J_{\mathrm{Se-P}} = 50.1 + 256\mathrm{EN}$	0.97	Pauling	1
$J_{\mathrm{Se-P}} = 133 + 228\mathrm{EN}$	0.97	Allred–Rochow	1
$J_{\mathrm{Se-P}} = 123 + 233\mathrm{EN}$	0.95	Sanderson	1
$J_{\mathrm{Se-P}} = -12.5 + 279\mathrm{EN}$	0.97	Pauling	3
$J_{\mathrm{Se-P}} = 83.0 + 246\mathrm{EN}$	0.96	Allred–Rochow	3
$J_{\mathrm{Se-P}} = 76.5 + 254\mathrm{EN}$	0.98	Sanderson	3

[a] Obtained by averaging the electronegativities of the substituent atoms on phosphorus.

$$J_{\mathrm{Se-P}} = -8345.2 + 3.88\nu(\mathrm{BH(asym)}) \qquad (r^2 = 0.98) \qquad (1)$$

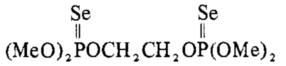
$$J_{\mathrm{Se-P}} = -13.769 + 6.28\nu(\mathrm{BH(sym)}) \qquad (r^2 = 0.85) \qquad (2)$$

$$J_{\mathrm{Se-P}} = -9839.1 + 4.53\nu(\mathrm{BH(wtd\ av)}) \qquad (r^2 = 0.97) \qquad (3)$$

Recently the increase in $J_{\mathrm{H-P}}$ of the $\mathrm{HP(OR)_3^+}$ analogues of $\mathrm{SeP(OMe)_3}$ and **1–4** (i.e., Se replaced by H$^+$) has been connected via CNDO/2 calculations to the accumulation of positive charge on phosphorus upon increasing constraint.[33] Moreover, this increase in charge can be qualitatively rationalized in terms of lone pair orbital repulsion and rehybridization effects.[33,37] Because there are no π contributions in the H–P bond, the Fermi contact contribution (which contains an atomic charge term) is likely to be dominant in $\mathrm{HP(OR)_3^+}$ systems.[33] Since there is a linear relationship between $J_{\mathrm{H-P}}$ and $J_{\mathrm{Se-P}}$,[38] as shown in eq 4, the claim[3] that the latter coupling is likely to be dominated by the Fermi contribution is substantiated.

$$J_{\mathrm{Se-P}} = -309.5 + 1.51J_{\mathrm{H-P}} \qquad (r^2 = 0.91) \qquad (4)$$

Interestingly the rise in $J_{\mathrm{Se-P}}$ upon constraint of an acyclic selenophosphate to six- and five-membered ring analogues was not apparent from data in the literature owing to the previously reported[19] low value for **2** (948 Hz). We believe our value of 1011 Hz for this compound to be the correct one for the reasons given in the following argument. Our preparation leads to a product whose low-resolution mass spectrum contains a parent ion peak for **2** (m/e 202) which is more intense (by a factor of 9.4 at 20 eV) than that of the peak at m/e 406 which we attribute to **10**. This product could easily arise by



$$\mathrm{(MeO)_2\overset{\overset{\displaystyle Se}{\|}}{P}OCH_2CH_2O\overset{\overset{\displaystyle Se}{\|}}{P}(OMe)_2}$$

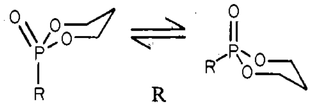
10

transesterification of the more strained **2**. The preparation of **2** reported earlier occurs under more vigorous conditions and the ^{31}P spectral data associated earlier with this species ($\delta(^{31}\mathrm{P})$ = 77.0, $J_{\mathrm{Se-P}}$ = 948 Hz)[19] corresponds closely to those we assign to **10** ($\delta(^{31}\mathrm{P})$ = 78, $J_{\mathrm{Se-P}}$ = 953 Hz). Thus passage of our product through an alumina column (in an attempt to purify it above the >90% purity indicated by its ^{31}P NMR spectrum) resulted in a growth of the ^{31}P resonance at 78 ppm at the expense of the peak at 88 ppm which we assign to **2**. At the same time, the ratio of **2** to **10** in the mass spectrum decreased from 9.4 to 1.6 at 20 eV, suggesting that **2** is unstable with respect to **10**. The mass spectral studies also show a growth in a peak at m/e 217 after the alumina column treatment, which is indicative of the loss of a $\mathrm{OP(Se)(OMe)_2}$ fragment from **10**. It should be mentioned that the mass spectral peaks quoted are those for the species containing the most abundant selenium isotopes. Compound **10** is strainless and therefore would be expected to exhibit a $J_{\mathrm{Se-P}}$ value closer to that of acyclic selenophosphates. The above results support this belief. Thirdly, the high coupling value for the monomer (1011 Hz) fits the correlations of $J_{\mathrm{Se-P}}$ with ν(BH) of the borane phosphite analogues and $J_{\mathrm{H-P}}$ of the protonated phosphite analogues.[33]

$J_{\mathrm{Se-P}}$ and Conformational Equilibrium. Assuming that the $J_{\mathrm{Se-P}}$ values for **1a** and **1b** represent the couplings expected for the analogous conformers of **9**, it is possible to calculate a ratio of conformers in the equilibrium shown for **9** in the introduction. Taking the coupling constant of **9** (985 Hz) as the time average of the two chair conformers,[39] we obtain a ratio of 0.77 via eq 5, which is comparable to the values for

$$996[\mathbf{9a}] + 949(1 - [\mathbf{9a}]) = 985 \qquad (5)$$

the equilibrium of the analogous phosphate conformers **11a** and **11b** (0.6–0.8) derived by other techniques.[39] In a similar manner a **12a** to **12b** ratio of 0.80 can be calculated from the H–P coupling constants[39] of **12** and the rigid isomer analogues of **12a** and **12b** equatorially substituted in the 4,6 positions. The ratio for **12a** to **12b** obtained in this way also compares well with the 0.6–0.8 values obtained earlier using other approaches.[39] It thus appears that in six-membered ring systems, directly bound NMR-active nuclei can be effectively utilized to calculate conformer ratios. While $\delta(^{31}\mathrm{P})$ values have been used successfully in calculating conformer ratios in related systems,[39] this does not appear to be the case for **9** since the values for **9**, **1a**, and **1b** in Table I suggest that **9b** is the strongly dominant conformer in contrast to the $^{77}\mathrm{Se}-^{31}\mathrm{P}$ coupling results. No reason for this anomaly is presently apparent.



	R	
11a	OMe	**11b**
12a	H	**12b**

$J_{\mathrm{Se-P}}$ and Electronegativity. Owing to electronegativity differences, $J_{\mathrm{Se-P}}$ decreases from **4** to **5** as is the case from $\mathrm{SeP(OMe)_3}$ to $\mathrm{SeP(NMe_2)_3}$ (Table I). The increase in $J_{\mathrm{Se-P}}$ from **5** to **6**–**8** can be attributed to the increase in electronegativity of the $\mathrm{(NMe)_3PZ}$ portion of the cage compared to that of $\mathrm{(CH_2)_3CMe}$ in **5** although effects due to structural changes may also be operative. Within the series **6**–**8** it is tempting to postulate that there is an electronegativity increase of Z in the order NPh < Se < O. Although the positions of N and Se seem to be reversed, it should be noted that the phenyl group may depress the effective electronegativity of this group below that of selenium. Moreover, although the electronegativities of N and Se are quite different on the Allred–Rochow or Pauling scales,[40] they are substantially closer together when calculated by Mulliken's[40] or Sanderson's[41] methods. That the NPh group has a smaller electronegativity than oxygen is supported by calculations[42] which yield a value of 3.24 when oxygen is assigned a value of 3.55.

While the general effect of electronegativity on $J_{\mathrm{Se-P}}$ has been noted on previous occasions,[1,3,5,8] no quantitative expression for these correlations has been established. To this end we carried out linear regression analyses on two sets of data appearing in the literature.[1,3] The reason for not combining the sets is that although the correlation coefficients in Table II are seen to be very good, the slopes and intercepts of each of the scales are substantially different. It is not apparent why this should be so, although it may be noted that one set of data stemming from 29 compounds was obtained by continuous-wave methods (±6 Hz)[1] while the other set of data on 13 compounds was determined by a heteronuclear triple-resonance technique.[3] Any of the equations will, however, predict $J_{\mathrm{Se-P}}$ to within 4%. Thus despite the crude estimation of the substituent electronegativities by simply averaging the values for the substituent atoms, the correlations summarized in Table II are remarkably good and they should be useful for predicting $J_{\mathrm{Se-P}}$ values for new acyclic $\mathrm{SePZ_3}$ compounds.

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Registry No. **1a**, 68378-97-2; **1b**, 68421-53-4; **2**, 67761-25-5; **3**, 67471-54-9; **4**, 68378-98-3; **5**, 68378-99-4; **6**, 68379-00-0; **7**, 38167-29-2; **8**, 68379-01-1; **9**, 52912-90-0; $\mathrm{SeP(NMe_2)_3}$, 7422-73-3; $\mathrm{MeOPOCHMeCH_2CHMeO}$ (axial OMe isomer), 7735-86-6; $\mathrm{MeOPOCHMeCH_2CHMeO}$ (equatorial OMe isomer), 7735-82-2; $\mathrm{MeOPOCH_2CH_2O}$, 1831-25-0; $\mathrm{P(OCH_2)_3CMe}$, 1449-91-8; $\mathrm{P(OCH_2)_2COMe}$, 61580-09-4; $\mathrm{P(NMeCH_2)_3CMe}$, 14418-26-9; $\mathrm{MeOPOCH_2CH_2CH_2O}$, 31121-06-9; selenium, 7782-49-2; KSeCN, 3425-46-5; $\mathrm{SeP(OMe)_3}$, 152-19-2.

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Electron Spin Resonance Study of Manganese(II) Ions in Trigonal-Prismatic Coordination in Tris(acetylacetonato)metal(II) Anions

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ESR spectra are reported for manganese(II) ions doped into polycrystalline $M^I[M^{II}(acac)_3]\cdot nH_2O$ (M^I = Na, K; M^{II} = Co, Ni, Zn, Cd). Zero-field splitting parameters D and λ (=E/D) are derived, and the results are correlated with the distortions of the anions from octahedral geometry. For the cadmium compounds, the high values of D are consistent with trigonal-prismatic geometry, for $K[M(acac)_3]$ (M = Co, Ni) the results indicate near-octahedral structures, while for $Na[M(acac)_3]\cdot nH_2O$ (M = Co, Ni, Zn) intermediate values are obtained.

Introduction

In recent years ESR has been shown[1,2] to be a useful tool in determining the stereochemistry of manganese(II) complexes. Moreover, some attempts have been made to use this ion as a stereochemical probe for other divalent metal ions.[3,4] However, no investigations appear to have been made of the ESR spectra of manganese(II) ions in trigonal-prismatic coordination, in spite of the growing recognition of this geometry as a viable alternative to the octahedron in certain cases.

We report here an ESR study of manganese(II) ions doped into polycrystalline $K[Cd(acac)_3]H_2O$, which has recently been shown to have trigonal-prismatic geometry.[5] Further studies with other tris(acetylacetonato) anions as host lattices have been made for comparison.

Experimental Section

The complexes were prepared by the method of Dwyer and Sargeson[6] and had satisfactory analyses. The doping was 1% nominal, and the complexes were magnetically dilute. Attempts to prepare $K[Zn(Mn)(acac)_3]$ were unsuccessful.

All spectra were obtained on polycrystalline samples at room temperature. The spectrometers have been described previously.[7]

Spectral Results

Spectra were obtained at X- and Q-band for each of the doped complexes. The results were interpreted using the "simplified" spin-Hamiltonian (1) in which A and g are assumed isotropic, with g = 2.00. A first estimate for the values of D and E was made using first-order perturbation theory. The values were then refined by exact diagonalization of a spin Hamiltonian matrix based on (1) but omitting the hyperfine interaction term. The calculated energy levels were scanned using the program[7] ESRS.

$$\mathcal{H} = g\beta BS + D(S_z^2 - \tfrac{1}{3}S^2) + E(S_x^2 - S_y^2) + SAI \qquad (1)$$

The X-band spectrum of $K[Cd(Mn)(acac)_3]H_2O$ was exceedingly complicated, with a large number of overlapping transitions. The better resolution at Q-band was therefore necessary to an interpretation of the results. A good fit to this spectrum was obtained using the parameters D = 0.113 cm^{-1} and λ (=E/D) = 0.06 (Table I). Similar assignment at X-band is less useful, on account of both the serious overlapping of transitions and the mixing of wave functions, which occurs here.

Table I. Q-Band ESR Spectrum (mT) of $K[Cd(Mn)(acac)_3]\cdot H_2O$

	calcd for D = 0.113 cm^{-1}, λ = 0.06	
obsd (ν = 35.85 GHz)	B	axis, levels[a]
796 w	797	a_z
1005 ms	1009	e_y
1036 ms	1039	b_z
1085 ms	1098	e_x
1124 s	1129	d_y
1167 s	1168	d_x
1354 s	1361	b_x
1405 s	1408	b_y
1487 ms	1489	a_x
1517 ms	1522	d_z
1572 ms	1574	a_y
1764 w	1765	e_z

[a] Assignments are for negative D; see text.

Table II. Q-Band ESR Spectrum (mT) of $Na[Cd(Mn)(acac)_3]$

	calcd for D = 0.109 cm^{-1}, λ = 0.03	
obsd (ν = 35.815 GHz)	B	axis, levels[a]
828 w	813	a_z
1035 ms	1038	e_y
	1046	b_z
1085 ms	1081	e_x
1138 s	1143	d_y
1159 s	1162	d_x
1374 s	1369	b_x
1390 s	1391	b_y
1501 ms	1501	a_x
	1513	d_z
1532 ms	1541	a_y
	1746	e_z

[a] Assignments are for negative D.

The "best-fit" parameters from the Q-band spectrum were therefore used to simulate the random-orientation X-band

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