

X-Ray and NMR Studies of Vanadium(V)-Nitrilotriacetate Complex

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바나듐(V)-니트릴로트리아세테이트 착물의 X-선 및 핵자기공명 연구

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Abstract: New vanadium(V) complex, $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$, has been synthesized and its structure has been determined by solution and solid-state NMR spectroscopies as well as X-ray crystallography. The unit cell of the monoclinic crystals contains four complexes with $a=6.923(1)$ Å, $b=8.824(2)$ Å, $c=19.218(11)$ Å and $\beta=91.60(3)^\circ$ in the space group of $P2_1/n$. The $[\text{VO}_2\text{NTA}]^{2-}$ anion has distorted octahedral geometry with *cis*- VO_2 moiety. It is confirmed that the octahedral geometry is retained in both of solution and solid-state complexes.

요약: 새로운 바나듐(V) 착물인 $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$ 를 합성한 후, 용액 및 고체핵자기공명분광법 및 X-선회절법으로 그 구조를 측정하였다. 그 결과 단사결정구조(space group= $P2_1/n$)의 이 착물의 단위세포는 4 착물을 가지고 있으며, 그 파라미터는 다음과 같다: $a=6.923(1)$ Å, $b=8.824(2)$ Å, $c=19.218(11)$ Å, $\beta=91.60(3)^\circ$. 용액 및 고체에서 이 착물의 $[\text{VO}_2\text{NTA}]^{2-}$ 이온은 *시스*- VO_2 단위를 가진 찌그러진 팔면체 구조를 가지고 있음을 알 수 있었다.

Key words: vanadium(V) complex, nitrilotriacetate, X-ray crystallography, NMR spectroscopy.

1. Introduction

With the recent discoveries of the first two naturally occurring vanadium-containing enzymes, the bromoperoxidase and nitrogenase, the coordination chemistry and reactivity of vanadium is receiving renewed attention.¹ Of various ligands many carboxylates are known to form anhydrides with vanadate in solution, if they have additional hy-

droxyl or amine groups available for chelation. Oxalate²⁻⁴ gives simple mono- and bis-oxalato octahedral complexes, presumably with *cis*- VO_2 species. Also aminopolycarboxylate, such as ethylenediaminetetraacetate(EDTA) forms similar octahedral complex with *cis*- VO_2 species.⁵⁻⁸ However, α -hydroxycarboxylates such as lactate, glycerate etc. form a variety of derivatives, including simple esters, chelates having trigonal bipyramidal coordi-

nation, and two binuclear complexes with mixed coordination.^{3,9,10}

The solid vanadium(V) complexes of oxalate^{11,12} and EDTA,^{13,14} in which the anion has irregular octahedral geometry with two double-bonded oxygen atoms, are known to have a *cis*-VO₂ core from X-ray diffraction studies.

To understand chemistry of vanadium and to develop new chelating agents for the quantitative determination of vanadium, we have studied the interaction of vanadium(V) with some aminopolycarboxylates in aqueous solution by multinuclear NMR spectroscopy. In the previous paper,¹⁵ we studied the chelate ring opening-closing process in (nitrilotriacetato)dioxovanadate(V) ion in aqueous solution by ¹³C NMR spectroscopy. In this paper we prepared new vanadium(V) complex, diammonium (nitrilotriacetato)dioxovanadate (NH₄)₂[VO₂NTA], and its structure was studied by the solution(¹H, ¹³C and ⁵¹V) and solid-state(¹³C) NMR spectroscopies. The spectra were discussed on the basis of the X-ray structure of the complex.

2. Experimental

2.1. Materials

Ammonium metavanadate(NH₄VO₃), nitrilotriacetic acid(H₃NTA), 25% ammonia water and D₂O were purchased from Aldrich Chemical Company. All reagent grade chemicals were used without further purification.

2.2. Preparation of vanadium(V) complex

The reaction of NH₄VO₃(0.02 mole, 2.34g) with H₃NTA(0.02 mole, 3.82g) and 25% ammonia water (0.02 mole, 1.3mL) in 100mL water produced yellow solution, which was filtered after being stirred for 3 hr. The solution was concentrated by passing a stream of dry air at room temperature for 2 days. The pale yellow crystals were formed and then filtered. The complexes were recrystallized from

water. The product was 1.95g(63.1%). The single crystals were obtained by slow evaporation from an aqueous solution of the product. Analytical data (chemical formula, VN₃O₅C₆H₁₄) of the complex was the same as follows: calculated(%): C 23.46, H 4.59, N 13.68, found(%): C 23.34 H 4.68 N 13.83.

2.3. X-ray measurements

Unit cell determination and data collection for X-ray crystal structure determination were performed on a Enraf-Nonius CAD4/Turbo automated diffractometer using Mo K_α radiation(λ = 0.71069Å). A piece measuring 0.5×0.5×0.5mm was cut from a larger single crystal and glued to a glass fiber with an epoxy resin. After the mounted crystal was centered in the X-ray beam, 25 reflections in diverse reciprocal space were centered by automatic search program and used to obtain cell parameters. After preliminary cell was determined, high-angle data(2θ > 20°) were collected and 25 of these reflections were centered and used to obtain more accurate cell parameters. Unit cell parameters and the systematic absences indicated the monoclinic space group P2₁/n(No. 14)¹⁶ with Z=4. Data were collected on this improved unit cell at ambient temperature up to 2θ=50°. Data reduction including correction for Lorentz-polarization, and decay and absorption were performed. Crystal structure was solved and refined with full-matrix least-squares by using programs from the Enraf-Nonius structure determination package. Data were collected according to the parameters in Table 1. The structure model was drawn using ORTEP, Oak Ridge Thermal Ellipsoid Plot Program.¹⁷

2.4. NMR measurements

¹H, ¹³C and ⁵¹V spectra of samples in D₂O were recorded on a JEOL GSX-400 NMR spectrometer at 400, 100.5 and 105 MHz, respectively, at 298 K. ¹³C spectra of solid samples(ca 0.2g) were recorded

Table 1. X-ray crystallographic parameters

Formula	VN ₃ O ₈ C ₆ H ₁₄
Formula wt.	307.1
a, Å	6.923(1)
b, Å	8.814(2)
c, Å	19.218(11)
β, deg	91.60(3)
V, Å	1172.1(7)
Z	4
d _{calc} , g cm ⁻³	1.714
Space group	P2 ₁ /n
Temperature	ambient
Radiation, Å ³	Mo K _α (0.71073)
Lin.abs coeff, cm ⁻¹	8.5
Scan mode	θ-2θ
2θ _{max} , deg	50
No. of obsd. refl.	1874
No. of variables	164
R _i ^a	0.049
R _w ^b	0.076
Goodness of fit ^c	2.60

$$^a R_i = \sum |F_o - |F_c|| / \sum F_o$$

$$^b R_w = [\sum_w (F_o - |F_c|)^2 / \sum_w F_o^2]^{1/2}$$

^cGoodness of fit = [$\sum_w (F_o - |F_c|)^2 / \sum (m-s)$]^{1/2},
wherem=number of observed data and s=number of variables.

on a Bruker MSL-300 spectrometer (75.47MHz) with CP/MAS technique at room temperature. A spectral width of 29411 Hz and an accumulation of 200 transients with an acquisition time of 0.85s were used. The contact time was 2ms and the delay between each scan was 5s. The ¹H and ¹³C chemical shifts are referred to external TMS. ⁵¹V shifts are referred to external VOCl₃.

3. Results and discussion

It is reported from the kinetic study¹⁸ that vanadium(V) formed 1:1 complex with NTA ($K_{VO_2NTA} = 10^{13.8}$ at 25°C). Nitrilotriacetate containing a nitrogen and three oxygen is considered to react with VO₂⁺ ion as a tetradentate ligand. The

synthesized vanadium-NTA complex is stable at room temperature and its synthesis is readily accomplished in good yield. Large single crystals were easily grown by slow evaporation of the aqueous solution and showed no evidence of twinning and other defects.

3.1. X-ray crystal structure

Unit cell parameters and the systematic absences indicated the monoclinic space group P2₁/n with Z=4. Therefore, the compound has a crystallographically imposed center of symmetry. The position of vanadium atom was determined from an origin-removed Patterson map and the other non-hydrogen atoms located and refined by using difference maps followed by least-squares cycles. Both decay and absorption corrections were applied and after calculation of the hydrogen atom positions and a full anisotropic refinement of the structure, a final R_i value of 0.049 and R_w of 0.076 were obtained. The selected bond distances and angles are given in Table 2.

The solid-state structure of the [VO₂NTA]²⁻ ion in the complex is remarkably symmetric as shown in Fig. 1. There is no interaction between adjacent complexes in the unit cell and the geometry about the vanadium(V) ion may be regarded as distorted octahedral. The anion [VO₂NTA]²⁻ has a slightly irregular octahedral geometry in which two oxo ligands are *cis* to each other as shown in oxalate^{11,12} and EDTA^{13,14} complexes. These two oxygens have short V-O bonds (1.653 and 1.613Å) which indicate strong multiple bond character. The O-V-O angle (107.1°) in VO₂ moiety is larger than 90° that is the standard octahedral value. The small difference (0.040Å) of V=O bonds observed in the unconstrained complex might be due to interactions with the asymmetric environments. The average V=O bond length (1.633Å) in the complex is shorter (1.648Å) than in EDTA complex.¹⁴ This would be consistent with the slight increase in O-V-O angle

Table 2. Selected bond distances and angles^a

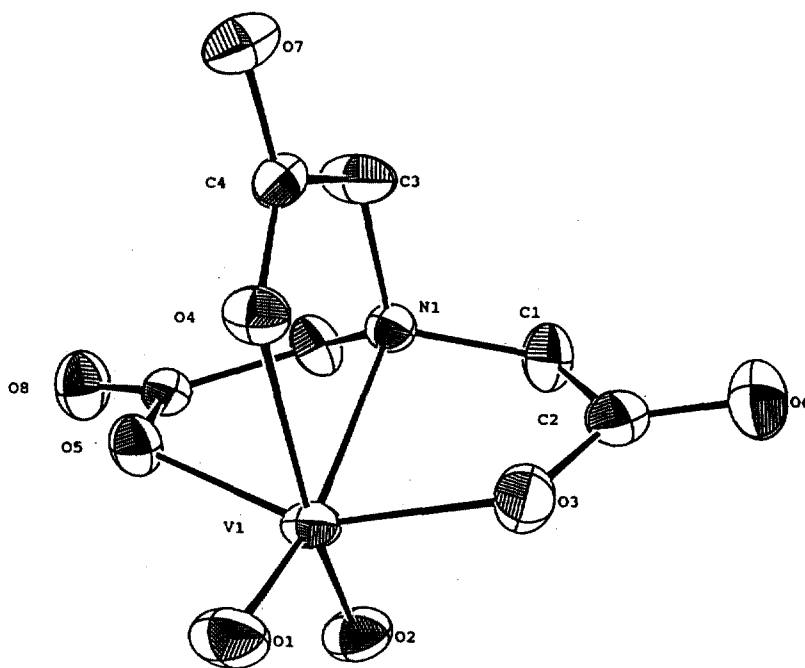
(a) Selected bond distances(Å)

Bond	Distance	Bond	Distance
V-O(1)	1.653(3)	V-O(2)	1.613(3)
V-O(3)	1.980(3)	V-O(4)	2.225(3)
V-O(5)	1.995(3)	V-N(1)	2.246(3)

(b) Selected bond angles(deg)

Bond	Angle	Bond	Angle
O(1)-V-O(2)	107.1(2)	O(1)-V-O(3)	99.2(2)
O(1)-V-O(4)	85.3(1)	O(1)-V-O(5)	103.2(1)
O(1)-V-N(1)	160.2(1)	O(2)-V-O(3)	96.8(2)
O(2)-V-O(4)	167.6(1)	O(2)-V-O(5)	94.1(2)
O(2)-V-N(1)	92.6(1)	O(3)-V-O(4)	81.8(1)
O(3)-V-O(5)	150.9(1)	O(3)-V-N(1)	77.6(1)
O(4)-V-O(5)	81.9(1)	O(4)-V-N(1)	75.0(1)
O(5)-V-N(1)	750.1(1)		

^aNumbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameters.

Fig. 1. ORTEP of $[\text{VO}_2\text{NTA}]^{3-}$ anion.

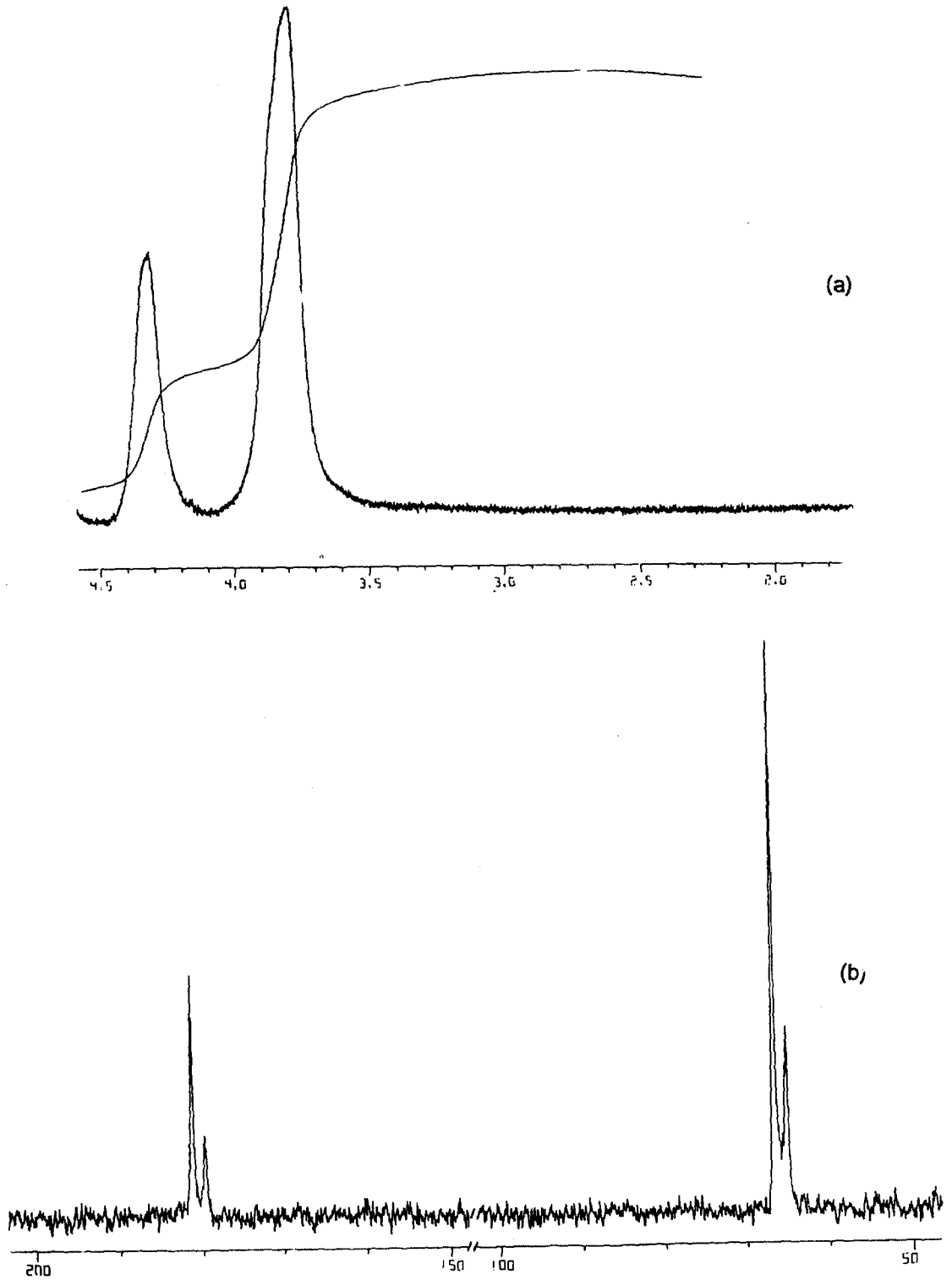


Fig. 2. (a) ^1H and (b) ^{13}C NMR spectrum of $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$ in D_2O .

from 106.96° in EDTA complex to 107.1° in NTA complex. The remaining four coordination sites of vanadium atom are occupied by a nitrogen atom and three oxygen atoms of the NTA ligand, giving three five-membered glycinato rings in the complex. Three oxygen atoms of the NTA ligand in the complex fall into two groups depending on whether or not they are *trans* to a V=O bond. The *trans* bond (2.225\AA) is significantly longer than the other bonds (1.980 and 1.995\AA), a good illustration of the structural *trans* effect. This lengthening (by average 0.237\AA) and weakening of V-O bond which is *trans* to the oxo ligands is similar to 0.23\AA in vanadium (V)-oxalate complex.¹¹ This σ bond strength weakening is reflected throughout the rest of the anion. The stronger of the inner C-O bonds are adjacent to the weaker of the V-O bonds. It is

assumed that the hydrogen bonding to the vanadyl oxygen atoms occurs in the complex, also giving unsymmetric V=O bond lengths. The longer of the non-equivalent V=O bonds is the one which has the stronger hydrogen bonding to it. The bond length of V-N is shorter in NTA complex (2.246\AA) than in EDTA complex (2.359 and 2.366\AA)¹⁴, indicating stronger bond in NTA complex. Short V-N bond would give some reduction of strain within the glycinato rings in the complex. Minor variation in lengths of C=O bonds can also be attributed to hydrogen bonding with ammonium ions. The oxygens of C=O groups are the atoms most influenced by the environment of the anion.

3.2. Solution NMR spectroscopy

^1H and ^{13}C NMR spectra of the complex in D_2O

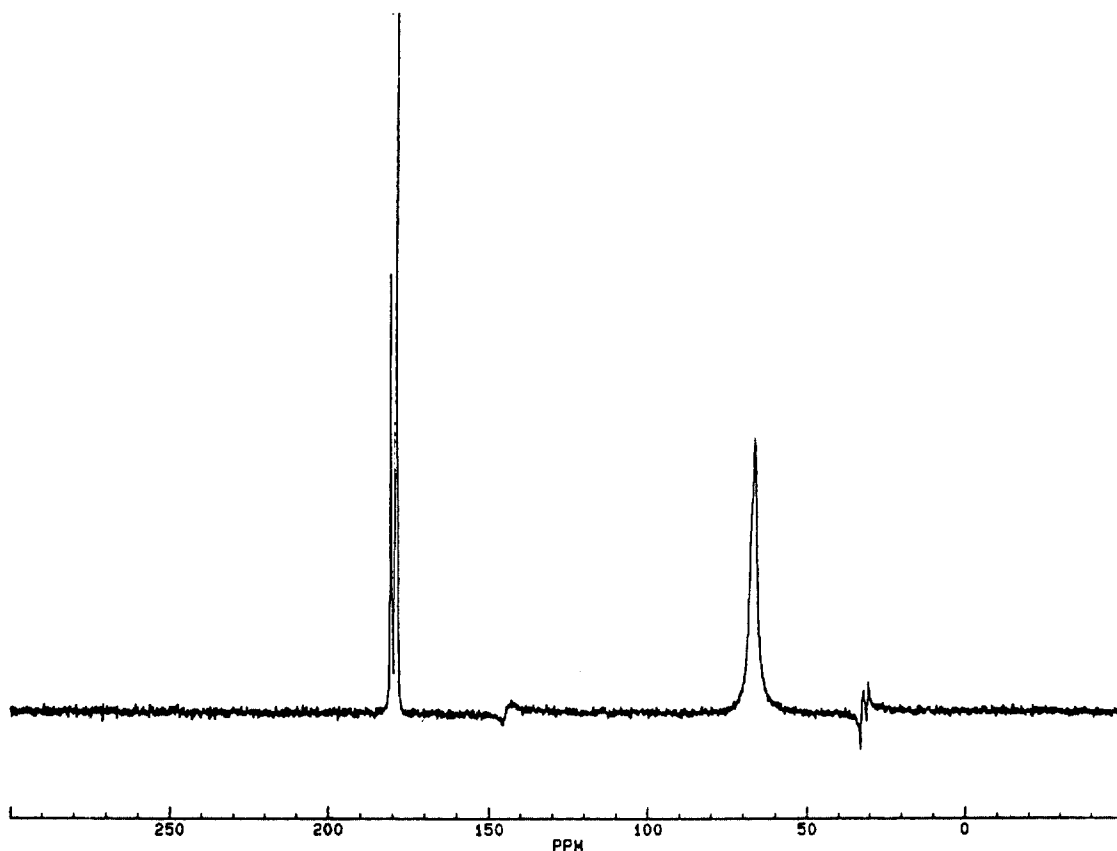


Fig. 3. CP/MAS ^{13}C NMR spectrum of the powder $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$.

solvent are shown in Fig. 2. In ^1H spectrum AB splitting patterns are expected for the glycinate groups in the complex. But two broad ^1H signals are observed at 3.78 and 4.31ppm which are assigned to *cis* to and *trans* to $\text{V}=\text{O}$, respectively, due to the short lifetimes of V-O and V-N bonds. When the lifetimes of both the metal-oxygen and the metal-nitrogen bonds are short, it is reported that the methylene protons of glycinate group are equivalent magnetically and give one resonance signal alone.¹⁹

In ^{13}C spectrum the complex shows two sets of glycinate groups at room temperature: one set(65.03 and 179.72ppm) is *trans* to $\text{V}=\text{O}$ bond and the other set(66.64 and 181.25ppm) is *cis* to $\text{V}=\text{O}$ bond. This indicates that a fast exchange between two types of the glycinate groups does not occur at room temperature on NMR time scale. But at elevated temperature the carboxylate group *trans* to $\text{V}=\text{O}$ bond will be easily broken and the exchange will occur faster, giving one set of glycinate signals.¹⁵

The complex shows ^{51}V peak at -504.3ppm, indicating octahedral coordination around vanadium atom. The half-width(430Hz) of ^{51}V peak is smaller than that(1000Hz) of EDTA complex⁸, due to increase of symmetry in the structure of NTA complex.

3.4. Solid-state NMR spectroscopy

CP/MAS ^{13}C spectrum of the powder $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$ is shown in Fig. 3. There are two sets of glycinate groups: one set(66.20 and 180.02ppm) is *trans* to $\text{V}=\text{O}$ bond and the other set (66.20 and 178.14ppm) is *cis* to $\text{V}=\text{O}$ bond. The peak assignment is based on the intensities of the peaks. The unit cell of solid complex has four crystallographically and magnetically equivalent molecules. This result is consistent with the X-ray structure. This indicates that the chemical exchange between two types of glycinate groups does not occur in the solid-state complex.

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